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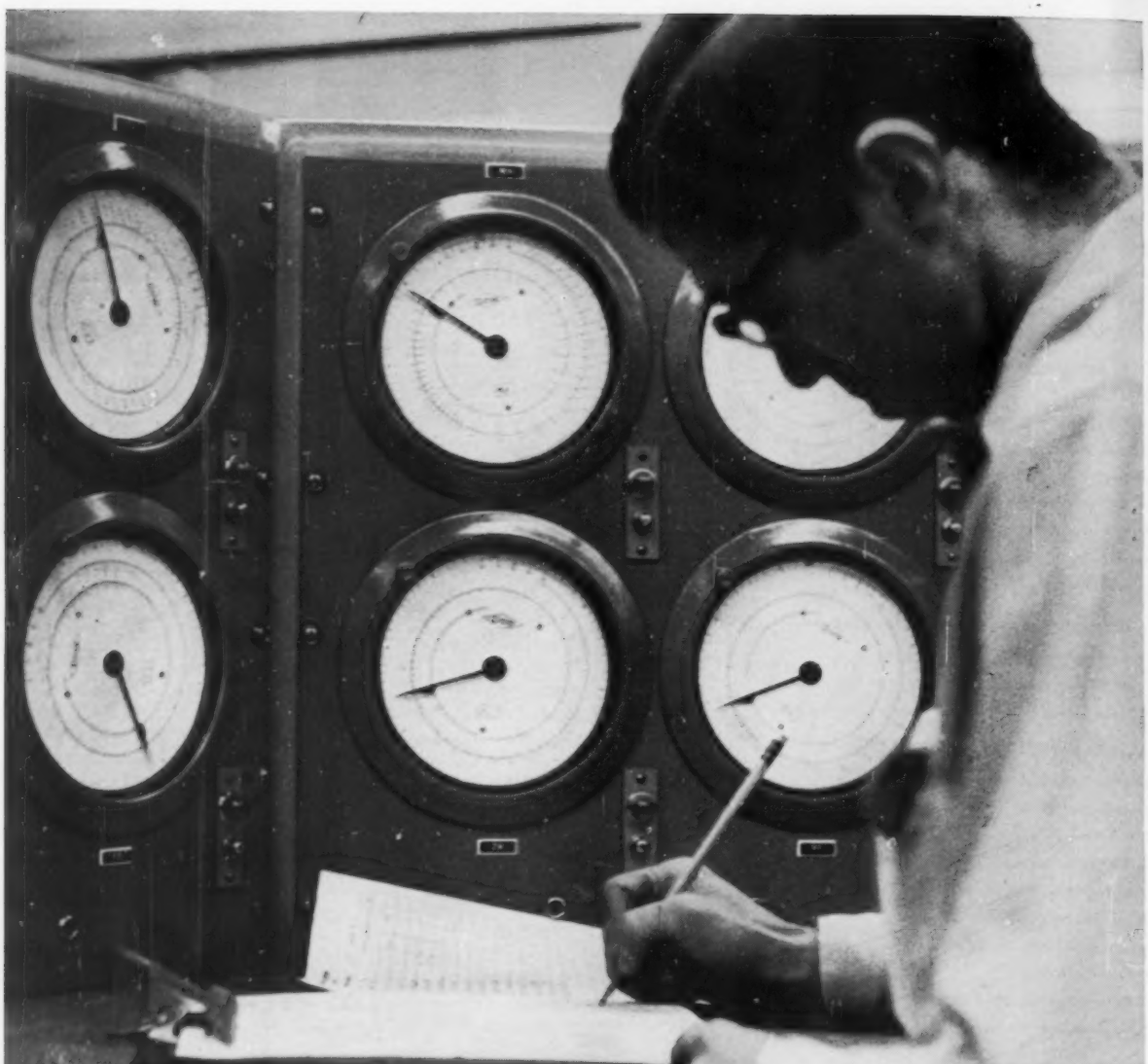

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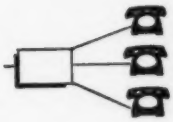
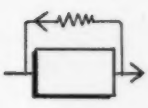
Electronic amplifier. First high-vacuum electronic amplifier. Made possible long distance telephony and then opened the way to radio broadcasting.



Wave filter. Precisely separates bands of frequencies. Provided major key to economical sharing of the same wires by many voices or radio programs. Indispensable control tool in radio, television and radar.



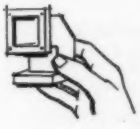
Negative feedback amplifier. Provides distortionless and stable amplification. Made possible the enormous, precisely controlled amplification needed in long distance telephone calls. The principle is now basic in high-quality amplifiers for radio, TV and high-fidelity reproduction.

Quartz crystal. Standard super-accurate quartz crystal oscillator developed for frequency controls in radio telephony. Has also become the standard control for clocks in world's astronomical laboratories.

Coaxial cable system. Hollow tube with a central conductor was developed to transmit hundreds of voices simultaneously. Now also provides long distance carrier for TV in partnership with microwave beams.

Transistor. Tiny solid-state device uses extremely small amounts of power to amplify signals. Makes possible electronic telephone switching and much smaller hearing aids, radios, TV sets and electronic computers.

Dial system "brain and memory." Takes over your call and sees that you are connected in the best and quickest way. Newest example: Direct Distance Dialing from home telephones to any part of the nation.



Waveguide. Hollow conductor transmits high-frequency waves. From this came the "pipe" circuits that are essential to radar and very short-wave radio communications.

Microwaves. Bell Laboratories developed long distance microwave transmission. It operates by focusing radio beams from station to station, carries cross-country telephony and TV.

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BELL TELEPHONE LABORATORIES

WORLD CENTER OF COMMUNICATIONS RESEARCH AND DEVELOPMENT

Editorial

Specifications

BELOW we reproduce page 1 of a nine-page government pamphlet of specifications:

MILITARY SPECIFICATION
LEAK TEST COMPOUND, OXYGEN SYSTEMS

1. SCOPE

1.1 Scope.-This specification covers 2 types of leak test compound.

1.2 Classification.-The leak test compound shall be one of the following types as specified:

Type I - For use in temperatures between, plus 160 degrees Fahrenheit and plus 35 degrees Fahrenheit.

Type II - For use in a temperature range of plus 35 degrees Fahrenheit to a minus 65 degrees Fahrenheit.

2. APPLICABLE DOCUMENTS

2.1 The following specifications, standards, and drawings, of the issue in effect on date of invitation for bids, form a part of this specification to the extent specified herein:

SPECIFICATIONS

Federal

NN-B-591	Boxes, Fiberboard, Wood-Cleated (For Domestic Shipment)
NN-B-621	Boxes, Wood, Nailed and Lock-Corner
TT-C-595	Colors; (For), Ready-Mixed Paints
LLL-B-631	Boxes; Fiber, Corrugated (For Domestic Shipment)
LLL-B-636	Boxes; Fiber, Solid (For Domestic Shipment)
PPP-B-566	Boxes; Folding Paper Board
PPP-B-585	Boxes; Wood Wirebound
PPP-B-601	Boxes; Wood; Cleated-Plywood
PPP-B-676	Boxes; Set-Up, Paperboard

Military

JAN-P-100	Packaging and Packing For Overseas Shipment, General Specification
JAN-P-103	Packaging and Packing For Overseas Shipment-Boxes; Wood Cleated; Solid Fiberboard
JAN-P-106	Boxes; Wood, Nailed (Overseas Type)
MIL-B-107	Boxes, Wood, Wirebound (Military Type)
JAN-P-108	Boxes, Fiberboard, Corrugated and Solid (Military Type)

The above may not convey much information to the uninitiated. Perusal of the succeeding eight pages gives only a few additional clues. Eventually one learns that the material in question should be shipped, ready for use, in small disposable squeeze-bottles, packed in suitable cartons. Far more economically a solid, or liquid, concentrate could be sent to the point of use, there to be made up to proper concentration. However, that would be like asking everyone to prepare his own soft drinks from the concentrated syrups. In the present case, the proper detection of leaks (in airplane fuel and compressed gas lines, for example) may be a question of safety, even of life, as well as of millions of dollars. It pays to make every effort to be sure that the technical personnel who do this work have every facility to do it well.

—CVK

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The specifications are based on the values determined in our laboratory from resistivity measurements of such crystals and resistivity measurements of floating zone refined bars cut from those crystals. Boron concentrations refer to those in the melt from which the characterization crystals are grown.

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NEW BOOKLET ON DU PONT HYPERPURE SILICON

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BETTER THINGS FOR BETTER LIVING
... THROUGH CHEMISTRY

Chemical and Electrochemical Properties of $FeSn_2$

Roger A. Covert and Herbert H. Uhlig

Corrosion Laboratory, Department of Metallurgy,

Massachusetts Institute of Technology, Cambridge, Massachusetts

ABSTRACT

Microhardness numbers of iron, tin, and $FeSn_2$ layers formed when iron is exposed to molten tin at 465°C show that the $FeSn_2$ layer is by far the hardest phase. It is also the most noble phase in acidified NaCl or dilute citric acid, both deaerated, as shown by micropotential measurements of the phases *in situ* or by measurements of bulk electrodes. Corrosion rates of $FeSn_2$ in the same media are too low to be easily measurable. Hydrogen overvoltage values for $FeSn_2$ at low current densities are intermediate between values for iron and tin. These properties are related to the predicted corrosion behavior of tin plate.

Although much attention has been paid to the corrosion behavior of commercial tinplate, very little work has been concentrated on corrosion properties of the alloy layer existing between the steel base and the tin surface. This alloy layer is reported to be composed essentially of $FeSn_2$ (1, 3). The present investigation was undertaken to study some of the properties of this phase and its possible role in the corrosion of tin-plated steel.

Some of the known properties of $FeSn_2$ include its density (7.743 g/cm³) (1); a rectangular acicular habit of the individual grains in the alloy layer (1); extreme brittleness in comparison to Sn or Fe (2); and porosity of the compound in the alloy layer (2). Several investigators (2, 3) have reported the relative inertness of $FeSn_2$ to attack by normal etching reagents, dilute aqua regia, and dilute nitric acid compared to the corrosion behavior of both Sn and Fe. However, experiments of Kohman and Sanborn (4) led to the conclusion that presence of the alloy layer was not helpful, and very possibly detrimental to the corrosion of tin plate. An explanation was not proposed.

In this investigation measurements of hydrogen overvoltage, corrosion potential, and corrosion rates in two aqueous media are reported. The interpretation of these data bear directly on the expected corrosion behavior of the alloy layer.

Experimental Procedure

Preparation of $FeSn_2$.—Attempts to prepare $FeSn_2$ by mixing the pure components in their correct stoichiometric proportions and melting in a He atmosphere were unsuccessful. Failure resulted from the fact that when a melt containing 80.95% Sn and 19.05% Fe is solidified there are several solid-liquid transformations which take place before 496°C (the temperature below which $FeSn_2$ is formed) is reached (5). These reactions result in the formation of various solid phases of the Fe-Sn binary system. Prolonged annealing at 470° ±10°C for 21 days did not homogenize the structure to single phase $FeSn_2$; therefore another approach had to be used.

According to Jones and Hoare (6), when a chemically clean surface of Fe is immersed for a time in liquid Sn below 496°C it is found to be coated with Sn and a layer of $FeSn_2$ between the Sn coating and the Fe surface. It would appear from the phase diagram that FeSn (68.0% Sn) and a primary solid solution of Sn in Fe would also be present. However, the rate of formation of FeSn and the diffusion rates of Sn into Fe below 496°C appear to be so slow compared to the rate of formation of $FeSn_2$ that the latter phase alone has been found.

By taking advantage of this situation, samples of $FeSn_2$ for metallographic examination, microhardness measurements and micropotential measurements were prepared by immersing cylinders of high purity Fe (>99.95% Fe) ¼ in. in diameter by ½ in. long in a bath of liquid Sn (>99.9% Sn) controlled to 465° ±10°C for periods of 50-100 hr. The high purity Fe and high purity Sn used here, and in all other phases of this work, were obtained from the Vacuum Metals Corporation and the Vulcan Detinning Company, respectively.

The Fe cylinders were prepared by abrading the surfaces through 4-0 metallographic polishing paper, degreasing in boiling benzene, pickling in concentrated HCl to remove the cold worked and contaminated surface, washing in distilled water, and drying in boiling acetone. The cylinders were dropped into the Sn bath immediately after drying in acetone, and a stream of He, which was purified by passing the gas over Cu chips at 500°C and through a liquid N_2 drying trap, was maintained continuously over the surface of the liquid Sn. After the cylinders were removed from the Sn bath, they were mounted in Bakelite perpendicular to their long axis and polished metallographically. A layer of $FeSn_2$ 0.001 in. to 0.005 in. thick was observed between the Fe and Sn phases.

For corrosion potential, hydrogen overvoltage, and corrosion rate measurements, $FeSn_2$ was prepared in a similar manner using a differently shaped specimen. Small rectangular plates ⅜ in. x ⅝ in. x ⅛ in. were abraded and degreased as before. Specimens were then placed in a Vycor transfer tube and heated to red heat in a stream of hydrogen, which was purified by passing the gas over Cu chips at 500°C and through a liquid N_2 drying trap, in

order to reduce any surface oxides. Specimens were then dropped with the aid of a magnet into a liquid Sn bath maintained continuously at 488° ±5°C without removing them from the hydrogen atmosphere and allowed to remain for 7-9 days. The edges of the plates were then ground away exposing the Fe base, which, along with the Sn surface, was dissolved in a 50 volume % solution of concentrated HNO_3. Two small plates of $FeSn_2$ remained, and electrodes and corrosion rate samples were prepared from these.

$FeSn_2$ prepared by the latter method was analyzed chemically and found to contain 19.9% Fe and 79.1% Sn compared to the theoretical values of 19.05% Fe and 80.95% Sn. A Debye-Scherrer x-ray powder diffraction pattern revealed that the major phase present was $FeSn_2$. However some faint lines of Sn and of some unidentified lattices were also present. The calculated *d* values for $FeSn_2$ compared favorably with the data of Nial (7). Considering the results of these two types of analyses, it was felt that the $FeSn_2$ samples contained more than 95% $FeSn_2$ with the remainder being Sn and FeSn.

Microhardness measurements.—The microhardness values of Fe, Sn, and $FeSn_2$ in the cylindrical samples were measured with a Tukon hardness testing instrument using a Knoop diamond indentor. Etching of the surface was not necessary, since the three phases were quite distinct. A typical photomicrograph is shown in Fig. 1.

Micropotential measurements.—Micropotential measurements of Fe, Sn, and $FeSn_2$ in deaerated 4% NaCl and HCl solution of *p*H 2.0 were made using essentially the same method as developed by Pingel (8). This procedure consists of washing the metallographically polished sample with distilled water and then acetone, and coating the entire surface with a transparent plastic composed of 10 parts by weight of ethyl cellulose, 20 parts petroleum ether, 60 parts toluene, and 20 parts ethyl alcohol. The coating dries readily in about 10 min and can be removed easily with benzene. Electrical contact with the mounted specimen was obtained by drilling through the side of the Bakelite mounting until contact was made with the metal sample. A 4 mm Pyrex tube was inserted into the drill hole and sealed in place of a 50% beeswax-50% resin wax. When cool, the wax was also covered with a plastic coating. A drop of Hg and a Cu wire were inserted into the Pyrex tube, the Hg making contact with the sample and the wire with the Hg. Indentations through the plastic coating to the specimen surface were made in the desired location with the Tukon hardness testing instrument using a Vickers diamond indentor. Indentor loads of either 25 or 50 g were used, depending on the thickness of the plastic coating.

Commercial pre-purified N_2 further purified by passing over Cu chips at 500°C was bubbled through the solution for at least 4 hr before measurements were made, in order to deaerate the solution. The *p*H was measured using a glass electrode.

The test solution was contained in a 250 ml Pyrex bottle fitted with a rubber stopper which had openings for the electrode, a salt bridge containing the same NaCl solution, the gas bubbler, and a gas exit tube. The salt bridge was in contact with a standard Ag-AgCl, 0.1*N* KCl electrode. For emf measurements a portable potentiometer was used in combination with an electronic *p*H meter employed as a high input resistance galvanometer.

After deaeration was complete, the electrode was inserted into the solution and measurements were taken every 3-5 min until such time as the plastic coating absorbed water and the potentials were no longer representative of the phase being investigated. This critical time was usually 45-60 min.

All measurements were made in an air thermostat maintained at 25° ±1°C.

Hydrogen overvoltage measurements.—Corrosion potential and hydrogen overvoltage characteristics for $FeSn_2$ and pure Sn were measured in deaerated 4% NaCl + HCl at *p*H 2.0 and dearated 0.1*M* citric acid solutions.

Tin electrodes ⅜ in. in diameter by ¾ in. long were prepared from the same high purity Sn that was used for the preparation of $FeSn_2$. The electrode design is shown in Fig. 2. Electrical contact with the sample was achieved by soft soldering a 1/16 in. drill rod to a 1/16 in. stem machined on the Sn sample. The drill rod was isolated from the solution by an 8 mm Pyrex tube fitted tightly in contact with the Teflon gasket, and which was held firmly in place by a machine screw with nut and washer silver

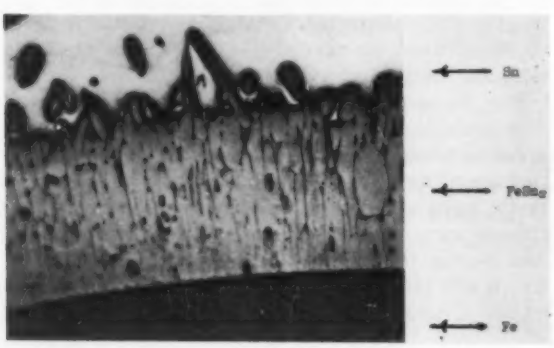

Fig. 1. Photomicrograph of $FeSn_2$ layer. 200X before reduction for publication.

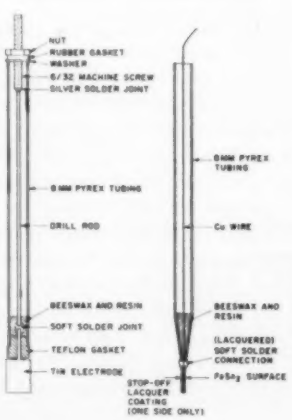

Fig. 2. Tin and $FeSn_2$ electrodes for corrosion potential and hydrogen overvoltage measurements.

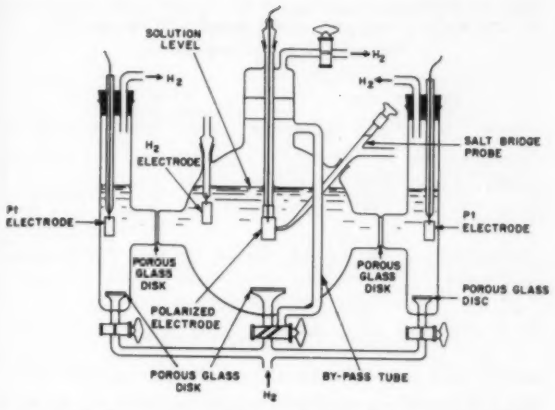

Fig. 3. Three compartment cell for hydrogen overvoltage measurements.

soldered to the other end of the drill rod. Only Sn, Teflon, and glass made contact with the solution.

$FeSn_2$ electrodes were made from plates of $FeSn_2$ described earlier. A fine Cu wire was soft soldered to one end of the plate and fitted into an 8 mm Pyrex tube with a capillary tip. The wire was sealed in place with 50% beeswax—50% resin wax. The capillary tip, soft solder connection, and one side of the specimen were coated with vinyl stop-off lacquer. This coating served not only to isolate the solder and Cu wire from the solution but also to protect the sample, which was extremely brittle and fragile.

The 3-compartment cell shown in Fig. 3 was used for all measurements. The center cathode compartment had a volume of 2200 ml and was separated from the 200 ml anode compartments by fine sintered glass disks. Since deaeration was accomplished by purified H_2, a platinized Pt electrode was inserted into the center compartment to be used as a reference electrode and for measuring pH.

The H_2 used for deaeration was purified by passing the gas over Cu chips at 500°C, a ruthenium catalyst at 300°C, and a palladium catalyst at room temperature. The NaCl solution was the same as was used for measuring micropotentials except for H_2 saturation instead of N_2 saturation. The citric acid solution was prepared from distilled water and reagent-grade citric acid.

Immediately prior to placing the specimen electrodes in the solution, the Sn electrode was abraded through 4-0 polishing paper, degreased in boiling benzene, pickled in concentrated HCl, and washed with distilled water. The $FeSn_2$ electrode was degreased with boiling benzene, pickled in concentrated HCl, and washed with distilled water.

In making a run, the solution was first deaerated for a minimum of 4 hr, then a smooth Pt electrode was inserted in place of the hydrogen electrode and the solution was cathodically pre-electrolyzed at a current density of 1 ma/cm^2 for 3 hr while deaeration continued. Then the specimen electrode, a salt bridge containing the same solution as in the cell, and the platinized-Pt electrode were inserted into the solution. The tip of the salt bridge was brought near to the electrode surface. Upon insertion of the electrodes, the potential of the sample was measured vs. the hydrogen electrode until a steady state was reached and maintained for at least 12 hr.

Hydrogen overvoltage was then measured at current densities of 0.1-1000 microamp/cm^2 by starting at the highest current density and reducing the current in steps of 1-min intervals to the minimum current density and then retracing the curve to the maximum again. Current was not shut off at any time during the run. Potentials in this case were measured against a saturated calomel electrode via the salt bridge using the same potentiometer circuit described earlier. During these runs H_2 was passed over the top of the solution via the by-pass tube shown in Fig. 3, and hence the solution was not stirred during measurements. A slight positive pressure of H_2 was maintained in the cell at all times.

Corrosion rate measurements.—Measurement of the corrosion rate of $FeSn_2$ was attempted in deaerated 4% NaCl + HCl, pH 2.0, and in deaerated 0.1*M* citric acid solutions without stirring. The electrolyte was placed in a 1500 ml spherical flask and was deaerated by bubbling purified H_2 through it for at least 4 hr before insertion of the specimens. Afterward H_2 was passed over the solution surface instead of bubbling through it.

The thin plates of $FeSn_2$, degreased with benzene and pickled in concentrated HCl as before, were placed immediately in small glass holders and immersed in the solution for periods of about five days. Because of the brittle, granular structure of $FeSn_2$, weight loss methods for measuring corrosion rates could not be used. There was always some mechanical breakage in handling the specimens. Therefore, since the corrosion products of Fe and Sn are both soluble in the solutions used, and both metals probably go into solution in the same proportion as in the metallic phase, the solutions were analyzed quantitatively for Fe alone by the orthophenanthroline colorimetric method (9). The amount of corroded metal vs. time was determined by analyzing 10 ml samples of solution twice daily.

Experimental Results

Microhardness measurements.—The maximum, minimum, and average Knoop hardness numbers for Fe, Sn, and $FeSn_2$ resulting from measurements made on four different samples are given in Table I.

A typical Knoop hardness number vs. distance plot for a tin-plate sample is shown in Fig. 4.

These results indicate, as expected, that $FeSn_2$ in the alloy layer is considerably harder than either Fe or Sn, thus supporting the contention that $FeSn_2$ is a hard, brittle phase that tends to break and crack during fabrication of tin plate. However, it

Table I. Hardness of Fe, Sn, and $FeSn_2$ phases found on Fe exposed to molten Sn

Phase	Number of readings	Knoop hardness number (100 g load) Minimum	Maximum	Average
Fe	14	76	127	96
Sn	5	7.7	10.5	9.4
$FeSn_2$	15	104	274	202

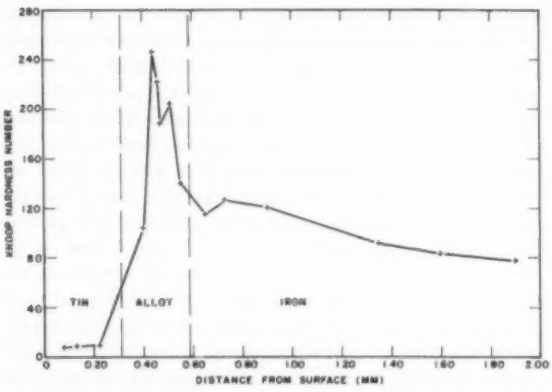

Fig. 4. Knoop hardness vs. distance for a tin-plated sample (100 g load).

should be remembered that the cold-rolled steel sheet used for making commercial tin plate is considerably harder than the soft high purity Fe used in these experiments and that consequently the magnitude of the difference between the hardness numbers of steel sheet and $FeSn_2$ is less.

The decreasing hardness of the Fe base as distance from the alloy layer increases seems to indicate that some Sn actually diffuses into the Fe lattice, thus increasing the hardness by alloying. This feature which is noticeable in Fig. 4 was characteristic of all specimens investigated. Decreased hardness of the compound at the phase boundaries probably results from diminished support at the edges, and is not real.

Potential measurements.—The micro-corrosion potentials *in situ* of Fe, Sn, and $FeSn_2$ and the corresponding corrosion potentials for separate Sn and $FeSn_2$ electrodes are given in Table II. The corrosion potentials for pure Fe, which were measured by Stern (10) in the same two media, are also listed.

The micro-corrosion potential and ordinary corrosion potential data for Sn and Fe were reproducible to ±3 mv while the data for $FeSn_2$ were reproducible to ±8 mv.

The relative potentials of Fe and Sn agree with previously reported data (1) indicating Sn to be more active than Fe in acid, oxygen-free environments. The data also indicate that $FeSn_2$ is the most noble of the three phases in these two media.

The importance of these potential relationships is discussed later.

Cathodic polarization.—If hydrogen is not removed by reaction with a depolarizer, hydrogen

Table II. Potentials of Fe, Sn, and $FeSn_2$ *in situ* on surface of Fe previously exposed to molten Sn, and comparative potentials of separate electrodes. All vs. standard H_2 electrode

Phase	Micro-corrosion potential *in situ* 4% NaCl + HCl, pH 2.0 V	Corrosion potentials of bulk electrodes 4% NaCl + HCl, pH 2.0 V	0.1*M* citric acid V
Fe	0.328	0.319 (Stern)	0.294 (Stern)
Sn	0.354*	0.351	0.361
$FeSn_2$	0.255*	0.287	0.271

* N_2-saturated solutions, others H_2-saturated.

Table III. Hydrogen overvoltage of Fe, Sn, and $FeSn_2$ in deaerated 4% NaCl + HCl, pH 2, and in deaerated 0.1*M* citric acid (average of 2 or 3 determinations)

Phases	4% NaCl + HCl, pH 2.0 a (v)	b (v)	i_o (amp/cm²)	0.1 *M* citric acid a (v)	b (v)	i_o (amp/cm²)
Fe (Stern)	0.90	0.100	1.1×10^{-7}	0.590	0.084	9.3×10^{-5}
Sn	1.10	0.14	1.4×10^{-6}	0.94	0.11	2.8×10^{-9}
$FeSn_2$	0.76	0.10	2.5×10^{-6}	0.96	0.14	1.4×10^{-7}

overvoltage η can be expressed by the Tafel equation (11):

$$\eta = a + b \log i, \text{ or}$$
$$= -b \log i_o + b \log i$$

where: a,b = constants, i_o = exchange current density (12), and i = applied current density. Using this notation, the averaged data for Fe [from Stern (10)], Sn, and $FeSn_2$ are given in Table III.

Typical overvoltage curves for Sn and $FeSn_2$ are given in Fig. 5 to 8. Values of the slope b for Sn were reproducible to ±0.015 v. The increase in slope of these curves near 0.1 ma/cm² is probably due to the approach of applied current to the limiting diffusion current for hydrogen ion discharge. This limiting current density was determined by Stern (13) to be between 1-5 ma/cm² for solutions of pH 2.

In general, measurements for Sn were the same whether current values were increased or decreased. For $FeSn_2$, however, the values on return to progressively higher current densities were higher than the values obtained in the initial measurements starting with high current density. This effect may be caused by organic impurities introduced by the wax sealant and the stop-off lacquer used to coat one side of the $FeSn_2$ electrode. These impurities were not present in the case of Fe or Sn.

Corrosion rate measurements.—No measurable amount of Fe was found in either the NaCl or the citric acid solution after $FeSn_2$ specimens had been exposed to these environments for 5 days. This would indicate that the corrosion rate of $FeSn_2$ is less than 3 mdd in these environments based on a minimum amount of iron of 0.02 μg/ml detectable by the electrophotometer and a total specimen area of 0.05 dm².

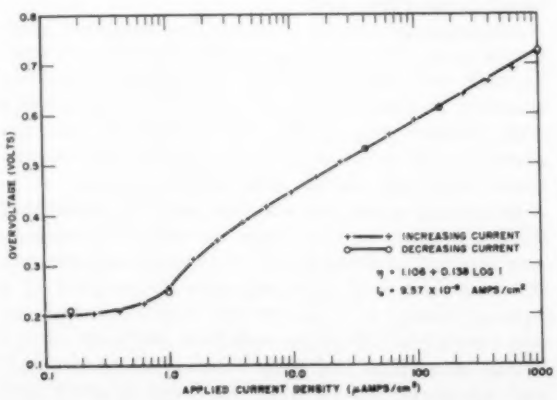

Fig. 5. Hydrogen overvoltage of Sn in deaerated 4% NaCl, pH 2.0.

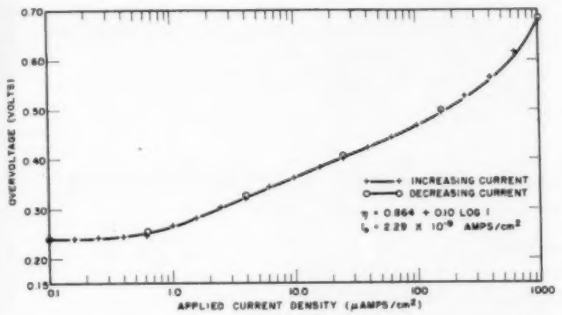

Fig. 6. Hydrogen overvoltage of Sn in deaerated 0.1M citric acid, pH 2.1.

A negative qualitative determination for Sn by the dithiol method (9) showed that Sn also did not go into solution to an extent detectable by this method.

Calculation of the corrosion rate of $FeSn_2$ from the hydrogen overvoltage and corrosion potential data by the method of Stern (10) gives values of 5.2 mdd and 6.6 mdd for $FeSn_2$ in the NaCl and citric acid solutions, respectively, provided $FeSn_2$ is assumed to corrode by the following reaction:

$$FeSn_2 \rightarrow Fe^{++} + 2Sn^{++} + 6e$$

This discrepancy between calculated and observed values is probably explained by the fact that the cathode surface of $FeSn_2$ is less than 100% of the surface as is assumed in the calculation.[1] How one can measure independently the actual cathode surface is not clear at present.

Since $FeSn_2$ is noble with respect to both Fe and Sn in the two media used here, an attempt was made to measure the anodic polarization characteristics of these two metals. However, the data were not reproducible and hence did not permit any definite conclusions.

Discussion

Certain qualitative conclusions are possible from the potential measurements. Since $FeSn_2$ is noble with respect to both Fe and Sn (Table II), it will act as the cathodic member when coupled with either of these two metals. Therefore, it becomes an undesirable substrate because it not only does not offer cathodic protection to Fe as does Sn, but it also ties up Sn which is thereafter not available to protect the Fe.

The hydrogen overvoltage of $FeSn_2$ in 0.1*M* citric acid at 10^{-5} amp/cm², for example, is 0.26 v compared with 0.39 v for Sn and 0.17 v for Fe. Hence the compound when coupled to Sn accounts for consumption of Sn at a lower rate than when an equal area of Fe is coupled to it. When the Sn is all consumed, the compound still exerts no accelerating effect on the hydrogen evolution reaction, because its overvoltage is higher than that of Fe. Therefore, the compound does not seem to be electrochemically deleterious to tin plate behavior for the described conditions of corrosion. The situation may differ, of course, when cathodic depolarizers are present, as is usually true with various foodstuffs. Behavior of the compound under depolarizing conditions requires further study.

[1] Hydrogen-overvoltage measurements are conducted typically at cathode current densities far above local-action current densities, and hence at values that polarize all the electrode surface. On the surface of a corroding metal, however, only part is cathode, the remainder being anode. For Fe in deaerated solutions, practically all the surface is cathode so that calculated and measured corrosion rates as carried out by Stern are in good agreement. Were the anode area larger, the cathode area of the corroding surface would polarize more than is assumed for 100% cathodic area; hence for this situation the measured corrosion rate is less than the calculated value.

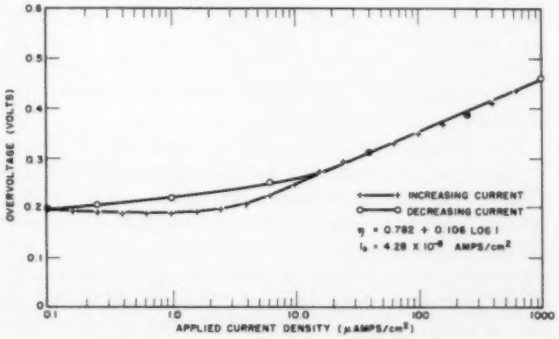

Fig. 7. Hydrogen overvoltage of $FeSn_2$ in deaerated 4% NaCl, pH 2.0.

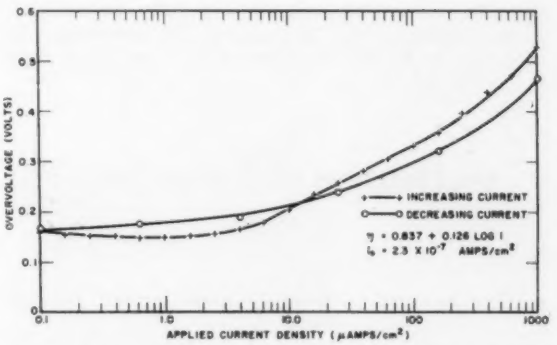

Fig. 8. Hydrogen overvoltage of $FeSn_2$ in deaerated 0.1M citric acid.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1958 JOURNAL.

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Nucleation of Crystalline Ta_2O_5 During Field Crystallization

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ABSTRACT

Nucleation during field crystallization of amorphous Ta_2O_5 films occurs at heterogeneities on the metal surface. The time between the application of the field and the appearance of the first crystals corresponds to growth to critical size of a crystal on one of the nucleation sites. The logarithm of the incubation period increases linearly with decreasing electric field at constant temperature. Possible mechanisms for the nucleation of crystals under these conditions are discussed.

Crystallization of amorphous anodic Ta_2O_5 films may be accomplished at temperatures in the vicinity of room temperature provided that a strong electric field is present in the film (1). This process results in roughly circular crystalline areas consisting of wedge-shaped polycrystalline segments, each area being surrounded by coiled cylinders of the replaced amorphous film. Recent observations of crystalline regions of similar appearance have been made on aluminum oxide anodic films (2), on hafnium oxide anodic films (3), on corrosion films on copper (4), and on chromium oxide (5) formed in oxygen. In addition, it has been observed here that an anodic Ta_2O_5 film crystallizes in a similar manner if heated to 590°C for about 20 min.

According to the mechanism proposed earlier (1) the crystalline areas grow radially by pushing aside the amorphous film present initially. The factors influencing the radial growth rate have already been discussed, and it is felt that such growth is qualitatively fairly well understood. It is the purpose of this paper to discuss some experiments which have been performed in order to determine the cause of the long incubation period before the first crystalline areas are observed.

Nucleation Sites

The fact that the time at which the first crystals are observed depends on the surface preparation (1) makes it appear likely that heterogeneities on the surface are nucleation sites. Further experiments of two types have confirmed this idea.

In one, an anodic film was held at one voltage until crystallization was about 50% complete, and the voltage was then raised rapidly to a somewhat higher voltage to allow further crystallization. It was found that if the rate of growth of the amorphous oxide film during the voltage increase was sufficiently rapid (greater than 40 Å/sec) most of the crystals formed at the lower voltage would not continue to grow at the higher voltage. The incidence of crystallization on the remaining area was observed as a function of time at the higher voltage, and a comparison was made between the number of new nuclei on this area and on a fresh specimen with no crystals present initially. It was found that far fewer crystals formed on the specimen which had first been partially crystallized at the lower voltage. For example, a specimen was held at 99°C, 100 v[1] until 50% of the area was crystalline. The voltage was then raised rapidly to 140 v and held for 550 sec, after which about 45 new crystals were observed in the total area under the microscope at a magnification of 100 diameters. Most of these new crystals occurred adjacent to crystals already present, and only a few, perhaps 5 or 10, formed at sites clearly removed from the original crystals. A specimen held 550 sec at 140 v without previous low voltage crystallization had 800 crystals in the area visible at 100 X, or about 400 crystals in an area equal to the noncrystalline area of the other specimen. The total number of crystals formed at both 100 v and 140 v on the first specimen was about 750 in the total area visible at 100 X.

It appears that there were a certain number of crystallization sites with a range of potencies available on the surface of each specimen. For the first specimen the most active of these sites were used up at 100 v and most of the resulting crystals made inactive for further crystallization by the rapid voltage increase to 140 v. Nucleation at 140 v on the remaining area was thus greatly retarded compared to nucleation on the second specimen which still contained all the most active sites.

The second type of experiment consisted of photographing a selected area before any oxide film was formed on the specimen and again after partial crystallization to see whether visible defects existed on the original surface at sites where crystals later occurred. Fig. 1 and 2 show such "before-and-after" pictures of an area of a specimen for which the crystallization treatment was 100 v, 99°C, 600

[1] The electrolyte used in all tests described in this paper was 2% HNO_3.

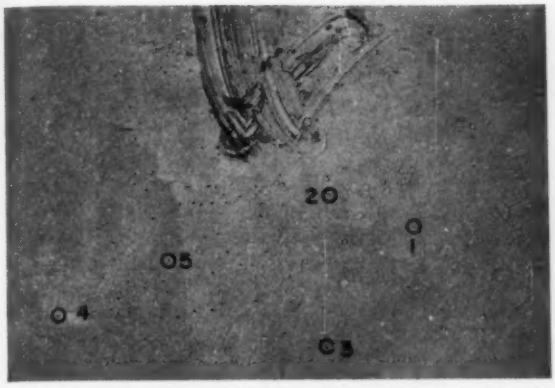

Fig. 1. Photomicrograph of Ta surface as chemically polished. 100X before reduction for publication.

sec. A total of 31 crystals were counted excluding those which occurred at the scratch introduced as a reference mark. Spots were observed on the original metal surface at all but three of the sites at which these crystals appeared. A few of these sites are indicated on both photomicrographs.

These experiments indicate that surface heterogeneities act as nucleation sites for field crystallization. Since there was no tendency for nucleation to occur at grain boundaries it is probable that the nucleation sites are inclusions of high impurity content. Crystallization of anodic films formed on evaporated Ta provides evidence that impurities are important. Tantalum films about 2000A thick were evaporated on one side of Ta strips of the type used for the other experiments. Crystallization of the resulting specimens showed that nucleation was far slower on the evaporated side. At 99°C, 100 v crystals were observed on the nonevaporated side after 300 sec, while none was observed on the evaporated side until 1000 sec. After 6500 sec the side without evaporated Ta was 90% crystalline, while only 1 or 2% of the evaporated side was crystalline. Fig. 3 shows a photomicrograph on an area part of which was shielded during evaporation. Very few crystals appear in the evaporated region, while the shielded region is almost completely crystalline. Only part of this change in crystallization rate can be attributed to decreased nucleation rate, since the growth rate

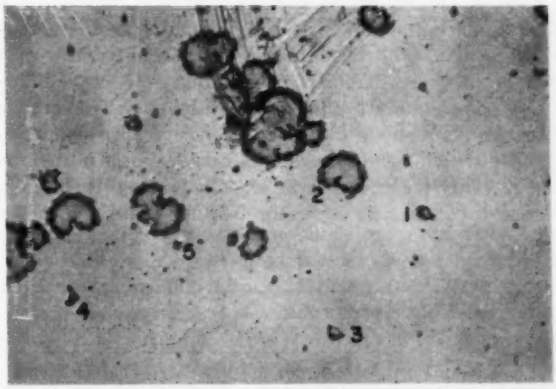

Fig. 2. Photomicrograph of same area shown in Fig. 1 after anodic oxidation for 600 sec at 100 v 99°C. 100X before reduction for publication.

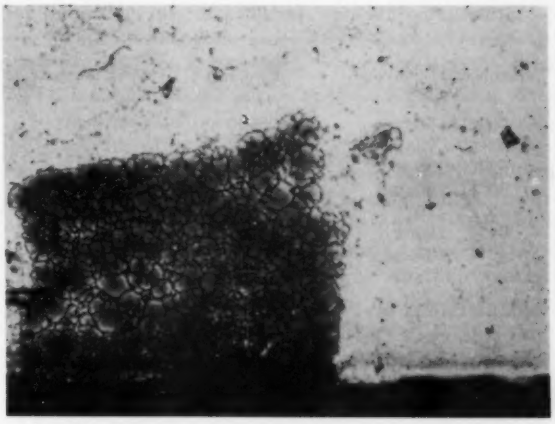

Fig. 3. Comparison of crystallization on evaporated Ta (white area) and on rolled chemically polished Ta sheet (lower left).

of the crystalline areas was also less on the evaporated side.

Effect of Voltage and Temperature on Incubation Time

Earlier data had indicated that there was a thickness dependent critical electric field for a given voltage and temperature above which crystallization did not occur (1). These data were obtained in experiments in which a constant voltage was applied to a specimen held at 99°C in 2% HNO_3 until crystallization occurred. It was found that crystallization did not occur until the thickness had grown sufficiently so that the field reached a certain value. An experiment to test the critical field hypothesis would be to form a film at a low temperature (where crystallization is extremely slow) to such a thickness that the critical field would be reached immediately at the start of the test at the higher temperature and desired voltage. When such experiments were performed, it was found that there was an even longer delay time before the start of new crystals than there had been previously. During this incubation period the field fell to values far below the field at which crystals were observed in earlier tests. In other words, there was no critical field for nucleation.

From a series of such tests at different voltages, however, it was found that the quantity of electricity passed through the cell from the start of the experiment to the time at which the first crystals were observed was approximately constant. Table I shows the number of coulombs passed through the cell from the start to the incubation time[2] for various voltages and temperatures, along with the observed nucleation times. It may be seen that the number of coulombs is roughly constant for all voltages at 99°C, and that there is an indication of an increase in the number of coulombs as the temperature is lowered. The apparent critical field was the result of the fact that the passage of a given quantity of electricity results in a greater percentage change in thickness for a thinner initial film. There was thus a greater decrease in the field at which

[2] The author defines incubation time to be that time at which the first crystals are observed.

Table I.

Experimental conditions	Nucleation time, sec	Total coulombs passed through cell
99°C, 50 v	5500	0.40
99°C, 70 v	600	0.39
99°C, 100 v	250	0.41
99°C, 140 v	130	0.44
99°C, 170 v	45	0.39
81°C, 100 v	750	0.44
47°C, 100 v	3500	0.55

crystals were first observed for specimens held at low voltages.

Experiments at Constant Field

Interpretation of the experiments described above is complicated by the fact that the amorphous oxide film grows continuously while the experiment is being performed, so that the electric field in the oxide is not constant. To eliminate this difficulty a series of experiments were performed in which specimens were held at constant field and constant temperature until crystallization occurred. All of the experiments were conducted using 2% HNO_3 as electrolyte, the temperature varying from 50° to 100° C and at 80-140 v. Each specimen was formed at the test temperature to a thickness sufficient to give the desired electric field strength at a convenient voltage. This voltage was then applied and the specimen was examined from time to time to determine when crystallization had just started. It was found that crystallization occurred in the same time at the same field regardless of film thickness or applied voltage.

Fig. 4 shows the results of these tests. It is clear that both lower temperature and lower electric field retard crystallization. At any one temperature the logarithm of the incubation time increases approximately linearly with decreasing applied field.

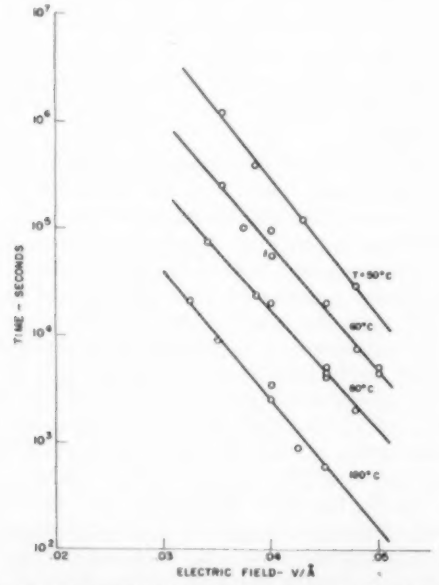

Fig. 4. Time required for the formation of the first visible crystals vs. applied electric field.

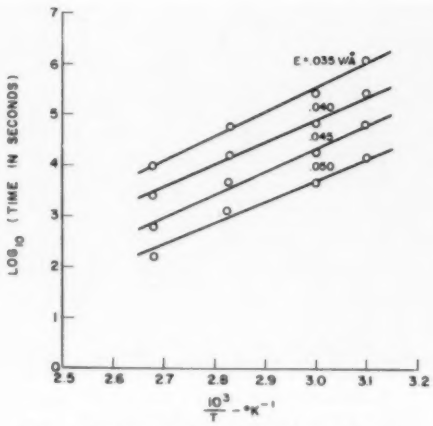

Fig. 5. Arrhenius plots of the data of Fig. 4

There is a considerable amount of scatter among the data, which is due to the difficulty of finding the very first crystals to form.

From these data the times at which crystallization started at various field strengths were obtained, and the logarithm of this incubation time was plotted against $1/T$ to obtain the activation energy (Fig. 5). The results of least square analysis of the data are shown in Table II.

It may be seen that there is a small decrease in activation energy with increasing electric field, and that the pre-exponential factor is approximately constant. The uncertainties in values given in Table II are rather large. The least square analysis shows that 50% of the measurements of activation energy would lie within an interval of about 2000 cal/mole on either side of the value given. Thus, the change of activation energy with field is not greater than the experimental error. The 50% confidence interval on the pre-exponential factor is about two orders of magnitude, so that the small variations reported are without significance.

Discussion

From the results of an electron microscope study reported earlier (1), it appears that a crystalline area begins rapid radial growth after a crack has been produced in the amorphous oxide film. Fig. 6 shows an electron micrograph of an area of a specimen on which crystallization had just started. The circular region in which a jagged crack in the amorphous oxide film is visible is apparently the first stage of crystallization, no smaller or less well developed regions having been observed. The cracks in the amorphous film are similar in appearance to those which can be produced by forcing a blunt object (such as the end of a pen-holder) through a sheet of paper. It is reasonable to assume that the

Table II.

Electric field v/Å	Activation energy, kcal/mole	Pre-exponential factor $(sec)^{-1}$
0.050	20.6	$1.6 \cdot 10^{-10}$
0.045	21.6	$1.4 \cdot 10^{-10}$
0.040	21.8	$4.5 \cdot 10^{-10}$
0.035	23.1	$2.5 \cdot 10^{-10}$

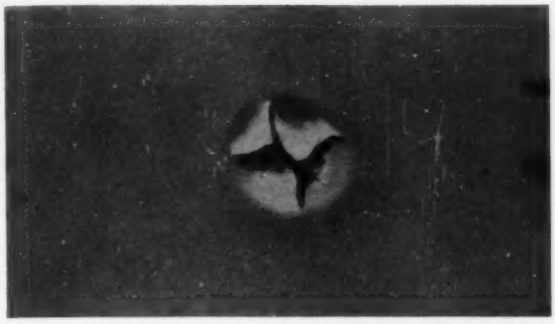

Fig. 6. Initial stage of recrystallization. 30,000X before reduction for publication.

cracks are produced by a crystal of Ta_2O_5 growing on one of the nucleation sites at the metal-oxide interface.

Two possible mechanisms are considered here for the initial growth of a crystal at a nucleation site, one in which crystallization of the already existing amorphous film occurs and the other in which completely new crystalline material forms underneath the amorphous film. Growth of new crystalline material underneath the amorphous film implies access of water to the metal under the film, presumably through pores in the amorphous oxide. The voltage drop in a pore of length 2000Å and of any diameter filled with electrolyte having a specific resistance of 100 ohm-cm in which the current density is 1 amp/cm^2 is $2 \times 10^{-5} \times 100 = 2.10^{-3}$ v. Hence, nearly all of the cell voltage (of the order of 100 v) would appear across the crystal growing at the base of the pore. Consequently a pore would be filled up almost immediately by extremely rapid growth of the crystalline or amorphous phase, and could have only a transient existence. This mechanism thus implies that there is a continuous formation and destruction of pores in a particular region or else that the pores are kept open by some process such as a vigorous gas evolution (which is not observed). It is difficult to see why there should be an incubation period which depends on field and temperature in the observed manner if pore formation is really the mechanism responsible for the initial crystal growth.

Crystal growth by transformation of the existing amorphous phase at a nucleation site seems far more likely. Stresses produced by a slight density difference in the two materials could eventually lead to a crack in the amorphous film. Once a crack was produced the solution would have access to the growing crystal which would then thicken rapidly and cause further cracking of the type observed. It is assumed that the incubation time for the formation of rapidly growing crystalline areas is the time required for a crystal growing on a nucleation site to reach the critical size necessary to cause a crack in the amorphous film. This incubation time is not a nucleation time in the ordinary sense of the term, since it is assumed that a stable crystal exists on the nucleation site at the start of the experiment. The nucleation time is the time required for this stable crystal to reach the critical size necessary to produce a crack. Presumably there would be a different critical size for each nucleation site depending on its size and configuration, but in these experiments the critical size is the same for all specimens since the first crystals observed would form on the most active type of site.

The rate of growth of the crystal is determined by the rate at which ions in the amorphous film can cross a potential barrier and assume lattice positions in the crystal. There exist strong electric fields in the two phases which can act to assist the ions in surmounting the potential barrier to their motion. The electric field at the position of the rate-determining step near a growing crystal may not be equal to the externally applied field because of differences in dielectric constant for the crystalline and amorphous phases or because of space charges which may result from unequal ionic mobilities in the two phases. For simplicity it is assumed that the field at the rate-determining barrier is proportional to the applied field.

The rate of growth of a crystal can now be calculated in terms of certain parameters suitable for comparison with experiment. The rate of motion of ions across a potential barrier in the presence of an electric field of such strength that jumps are overwhelmingly in the direction of the field is

$$R = A \exp - \left(\frac{Q - q\lambda E}{RT} \right) \qquad \text{(I)}$$

where A is a constant, Q the activation energy at zero field, q the charge on the ion, λ the distance from the equilibrium position to the top of the potential barrier, and E the electric field component in the direction of motion. To take account of the fact that field at the barrier may not be equal to the applied field it is necessary to use a proportionality constant defined by

$$E = f \cdot E_a \qquad \text{(II)}$$

where E_a is the component of the applied field in the jump direction. The rate of crystal growth is now

$$\frac{\Delta l}{\Delta t} = A \exp - \left(\frac{Q - q\lambda f E_a}{RT} \right) \qquad \text{(III)}$$

or since Δl is constant and equal to the critical size,

$$-\log \Delta t = \log A' - \frac{Q - q\lambda f E_a}{RT} \qquad \text{(IV)}$$

According to Eq. (IV) a plot of activation energy vs. electric field should give a straight line of slope $q\lambda f$. Fig. 7 shows such a plot, which has a slope of 7.2 in units of electronic charges times angstrom units. In view of the large uncertainty in the values of activation energy the value obtained for $q\lambda f$ could be in error by as much as a factor of two. A more accurate value may be obtained from the slopes of the curves shown in Fig. 2, using Eq. (IV). The values so obtained are 8.8, 7.8, 7.8, and 8.2 at temperatures of 100°, 80°, 60°, and 50°C, respectively. Taking $q\lambda f$ to be 8.2 the zero field activation energy, Q, is about 30 kcal/mole.

There are at least two ways in which the growth of a crystal nucleus could occur. In the first place

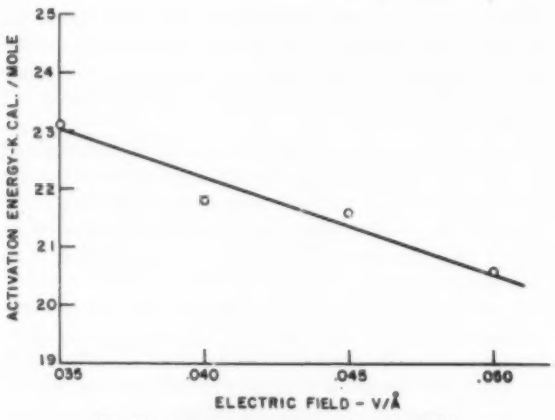

Fig. 7. Activation energy vs. electric field

oxygen and Ta ions could be transferred from the amorphous film to the crystal across the interface. Such a mechanism would require that the Ta ions move against the field, which is very unlikely at these fields and temperatures. A second possibility is that oxygen ions from the amorphous film are added to the crystal at the interface and that Ta diffuses out from the metal to the growing surface of the crystal. The Ta ions from the amorphous film would then be free to migrate through the film to the electrolyte interface and form more oxide. Such a mechanism would not have to proceed very long before a crack formed since such growth of the film at an isolated point would make it difficult to maintain contact at the oxide-metal interface without severe distortion of the oxide.

Assuming this mechanism to operate, the rate of crystal growth might be controlled by Ta ion migration in the growing crystal or in the amorphous oxide, or by oxygen ion migration across the crystal-amorphous interface. The zero field activation energy for ionic motion in the amorphous film at these fields is about 50 kcal/mole, which is considerably higher than the experimental value for nucleation. If $f = 1$, $q = 2$ (for oxygen ion migration) $2\lambda = 8.2$Å, which seems to be considerably too large. However, the values of Q and q (assuming $f = 1$) are reasonable for ionic conduction in crystalline Ta_2O_5. Gulbransen and Andrew (6) reported an activation energy of 27.4 kcal/mole for oxidation of Ta at temperatures where crystalline oxide is formed. If $q = 5$, $\lambda = 1.6$ so that the distance between equilibrium positions would be 3.2Å, a very reasonable value. A planned study of the kinetics of formation of crystalline tantalum oxide films should make it possible to tell whether ionic migration in the crystal is really the rate-determining step in crystal nucleation under these conditions.

Conclusions

1. Field crystallization occurs only at certain preferred nucleation sites at the metal-oxide interface. These sites may be inclusions of high impurity content in the metal.

2. The incubation period for the appearance of crystalline areas corresponds to the time required for a crystal growing underneath the amorphous oxide film to reach a critical size.

3. The logarithm of the incubation period increases linearly with decreasing electric field at constant temperature.

4. An incubation period consistent with experiment would result from control of the growth of the crystal by field assisted ionic motion. There is a possibility that the rate-determining step is Ta ion migration in the crystal.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1958 JOURNAL.

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Surface Protection and Selective Masking during Diffusion in Silicon

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ABSTRACT

An apparatus is described for the vapor-solid diffusion of donors and acceptors into silicon at atmospheric pressure. It consists essentially of a fused silica tube extending through one or more controlled temperature zones. A gas such as nitrogen carries the vapors from the heated impurity element or one of its compounds past the heated silicon.

At temperatures above about 1000°C, gases such as helium or nitrogen are shown to cause serious pitting or erosion of the silicon surfaces. A thin vitreous silicon dioxide envelope enclosing the silicon during the high temperature heating operation is shown to provide complete protection of the underlying surface against damage. Methods of obtaining surface passivation are described.

In addition to surface protection, a silicon dioxide surface layer also is shown to provide a selective mask against the diffusion into silicon of some donors and acceptors at elevated temperatures. Data are presented showing the masking effectiveness of the silicon dioxide layer against the diffusion of several donors and acceptors into silicon.

The application of the masking technique to produce precise surface patterns of both *n*- and *p*-type is described. An example of its feasibility in device considerations is illustrated by the construction of a transistor by double diffusion. This transistor is unique in that both the emitter and base contacts are made at the surface in adjacent areas.

Finally a new predeposition technique is described for controlling the impurity levels in diffused layers over wide ranges. Data are presented to illustrate this technique.

The vapor-solid diffusion technique has become of considerable interest recently for the introduction of selected conductivity type determining impurities into semiconductors. The application of this technique in the design of Si semiconductor devices is illustrated by the solar battery (1), power rectifiers (2), and high frequency transistors (3). The feasibility of producing such structures by vapor-solid diffusion resulted largely from the investigations of Fuller and his co-workers (4, 5). Their investigations provided the necessary information on the high temperature diffusion parameters required for controlling the impurity concentrations and depths of the diffused layers.

This paper describes: (*a*) a new apparatus for vapor-solid diffusion at atmospheric pressure, (*b*) some experiments illustrating surface protection of Si at high temperatures by oxidation, and (*c*) some experiments illustrating selective masking by SiO_2 surface layers against the diffusion of some impurities into Si at high temperatures. Methods for determining the electrical characteristics, surface concentrations, and diffusion depths are essentially the same as those described elsewhere (5) and are only identified in this paper.

Apparatus and Procedure

The apparatus for vapor-solid diffusion at atmospheric pressure is shown schematically in Fig. 1. It consists essentially of a fused silica tube extending through two controlled temperature zones. The first temperature zone serves to regulate the volatility of an impurity placed therein. The second temperature zone is the location of the Si samples. A rising temperature gradient between the two zones avoids the redeposition of the impurity vapor before reaching the Si samples. The temperatures are regulated to ±2°C by means of Pt-Pt 10% Rh thermocouples and automatic controllers.

The vapor from an impurity heated in the first temperature zone is carried past the Si heated in the second zone by carrier gases such as H_2, N_2, O_2, and CO_2 or mixtures thereof with or without the addition of water vapor. Flowmeters attached to one end of the furnace tube regulate the flow of the carrier gases. In this investigation flow rates of 1500 cc/min of the carrier gas were employed in furnace tubes of 2.5 cm ID. A temperature-controlled water bubbler is inserted between the flowmeters and the furnace tube when water vapor is being added to the carrier gas. Carrier gases were not saturated with water vapor under these flow conditions, but particular experimental conditions were found to be reproducible. The exit or open end of the furnace tube is inserted into a hood. This effectively removes the carrier gases which now probably contain residual amounts of 3rd and 5th column elements or their compounds. These in many cases are harmful poisons.

The Si samples are held vertically in a slotted fused silica plate as shown in Fig. 1. This assures a uniform contact of the carrier gas with both Si sur-

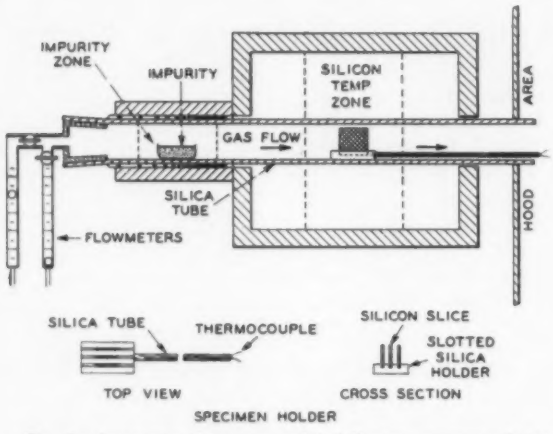

Fig. 1. Apparatus for vapor-solid diffusion at atmospheric pressure.

faces. A small silica tube fused to the sample holder is used to insert and remove the Si from the furnace. A Pt-Pt 10% Rh thermocouple inserted in the pusher tube is employed to measure the work temperature throughout the run.

Before the Si samples are inserted for diffusion or oxidation, the flow of carrier gas is started and allowed to continue for several minutes to establish a steady-state condition. The samples then are introduced at a reproducible rate into the desired temperature zone. At the end of the heating operation the samples generally are withdrawn at the insertion rate. In these experiments the samples were inserted and withdrawn in about 1 min.

Samples

The Si samples were cut from approximately 5 ohm cm *n*-type (arsenic doped) or *p*-type (boron doped) single crystal ingots grown in the [111] direction. The ingots were sawed perpendicular to the growth direction into slices approximately 10^{-1} cm thick. These were machine lapped on both surfaces with No. 1800 emery powder to a thickness of about 7×10^{-2} cm. After cutting into squares of 0.75 x 0.75 cm, the samples were etched for 4-5 min in a mixture of 5 parts of concentrated HNO_3 to 1 part of concentrated HF to produce a mirror finish. This resulted in final sample thicknesses of about 5×10^{-2} cm. Reproducible surfaces of excellent appearance were obtained by maintaining the etchant temperature at about 20°C and employing mechanical agitation during etching.

Surface Protection

When Si is heated in the previously described diffusion apparatus above about 1000°C for relatively short times in commercial grades of nonoxidizing gases such as H_2 or He, serious erosion or pitting of the surface occurs. A significant loss in weight also takes place. On the other hand, Si surfaces are essentially unchanged after long heating periods well above 1000°C in oxidizing gases such as O_2 and CO_2 or nonoxidizing gases containing sufficient concentrations of oxygen or water vapor.

The surface appearance of Si samples after heating in H_2, He, N_2, or O_2 gases is illustrated in Fig. 2. The surfaces were washed in concentrated HF after

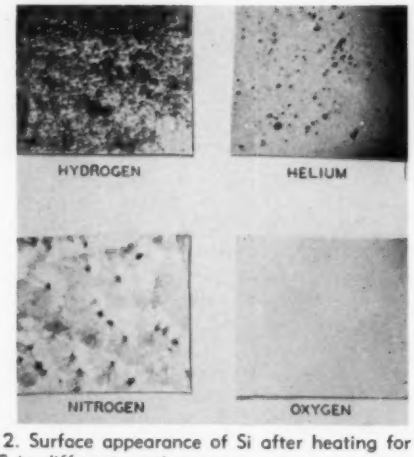

Fig. 2. Surface appearance of Si after heating for 1 hr at 1350°C in different carrier gases.

the heating operation to remove any surface layers such as SiO_2 which forms in the pure oxygen atmosphere. Note the damage on the Si surfaces after heating in H_2 and He. On the other hand after heating in oxygen the excellent surface appearance is essentially the same as that of the original etched surface. The crystalline surface appearance after heating in N_2 may be due to the formation of a Si_3N_4.

The effect of varying the water vapor content in a hydrogen carrier gas during heating on the surface appearance is illustrated in Fig. 3. The temperatures under the photographs represent the temperatures of the water bubbler. Note the decrease in the size of the surface pits as the water vapor content of the carrier gas is increased. Actually in this series of heating experiments at 1350°C, water bubbler temperatures between 30°-80°C resulted in excellent surfaces. However, a further increase in the water content of the carrier gas resulted in a large number of very small surface pits. The reappearance of surface pits might be explained by the failure to form a completely coherent oxide layer in the presence of high water vapor contents at this temperature. Silicon dioxide is known to be quite soluble in water at high temperatures.

Other examples of surface protection by oxidation might be given. For example, Si can be heated

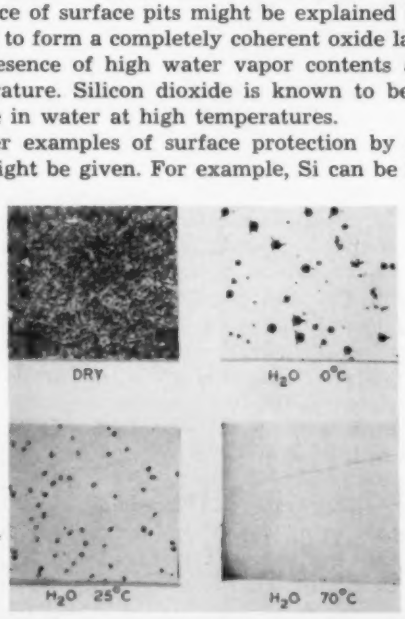

Fig. 3. Surface appearance of Si after heating for 1 hr at 1350°C in hydrogen containing different concentrations of water vapor.

in CO_2 or in various mixtures of N_2 and O_2 including air without apparent surface damage. The latter suggests many process simplifications for producing diffused junction layers. However, the oxidizing potential of the carrier gas must be sufficient so that the thermodynamic equilibrium favors the formation of SiO_2 at each processing condition. On the other hand optimum surface appearance does not necessarily result from maximum oxidizing conditions. Generally it is preferable to establish optimum conditions experimentally for each processing condition.

Surface protection of Si in oxidizing atmospheres is due to the formation of a continuous protective envelope of nonvolatile SiO_2. This prevents not only the evaporation of the underlying Si but also its complete oxidation. The oxide layer is easily removed by washing in HF. In this work the SiO_2 layers generally varied in thickness between about 1500 to 3000Å depending on the temperature, time and carrier gas composition. The layers exhibit brilliant interference colors. The constant thickness of the oxide layer on a particular Si surface is indicated by the uniformity of these interference colors.

Selective Masking

In addition to surface protection, a SiO_2 surface layer provides a selective mask at high temperatures against the diffusion of some donors and acceptors into Si. Only a few typical examples of selective masking will be given.

Masking is studied most effectively by preoxidizing etched Si slices and removing the oxide layer from one surface with HF. This provides an oxidized and unoxidized surface on the same sample for electrical, diffusion depth, and other measurements. In the examples reported here the preoxidation was done by heating at 1200°C for 1 hr in N_2 bubbled through water at 30°C. This gives an oxide layer about 2500Å thick.

Fig. 4 illustrates the masking of As by a SiO_2 layer at three diffusion temperatures. The first figure is a cross-sectional view of a p-type Si slice with an oxide layer on one surface. The next figure shows that arsenic trioxide is heated at 235°C and the carrier gas is N_2 bubbled through water at 30°C for each processing condition. In the next column the diffusion times and temperatures are given for each of the four processing conditions. The fifth column shows a cross-sectional view of the processed samples after a wash in HF which removes only the oxide envelope. The cross-hatching illustrates the relative thickness of the n-type conversion layer. The average sheet resistance values (ρ_s) and the diffusion depths (a) were measured by the four point probe and the 5 degree angle lapping-staining technique, respectively. These measuring techniques are described in some detail elsewhere (5). From the ρ_s and (a) values the surface concentrations (C_0) of the impurities given in the last column were calculated by assuming an error function distribution of the impurities through the diffused layers.

Note the absence of a conversion layer on the oxidized surface after the 1100°C diffusion shown in Fig. 4. This indicates that the surface concentration of the As on this surface is less than 3×10^{15} cm^{-3}, the background p-type doping in the original crystal. At the two higher diffusion temperatures a conversion layer is formed on the oxidized surface. However, the C_0 values remain relatively constant and well below those for the unoxidized surfaces. The effect of the SiO_2 surface layer and the diffusion temperature on surface concentration and hence diffusion depth is clearly evident from the data.

Fig. 5 illustrates the effect of carrier gas type on the diffusion of boron. The representations have the same significance as those described previously. Because of its very low volatility, the boron trioxide source is heated at the same temperature as the Si. Note the absence of a conversion layer on the oxidized surface and the highly doped conversion layer on the unoxidized surface after heating in oxygen. An appreciable masking effect by the oxide layer also is evident after heating in the nitrogen-water carrier gas. On the other hand no masking by the preoxidized surface is evident after heating in the hydrogen-water carrier gas. The doping level also is appreciably higher for the wet hydrogen than for the unoxidized surfaces in the other two carrier gases. The reason for this effect of carrier gas type and composition on the masking by SiO_2 surface layers is not known. However, it does suggest some difference in the molecular specie of the diffusant vapor in the various carrier gases which alters its reactivity with, diffusion through, or solubility in a SiO_2 layer. A complete study of the effect of carrier gas composition on the masking of a SiO_2 surface layer against the diffusion of donors and acceptors

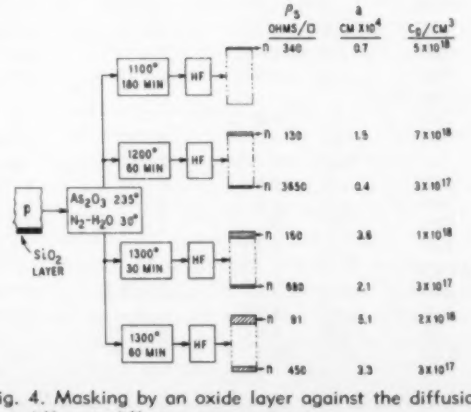

Fig. 4. Masking by an oxide layer against the diffusion of As at different diffusion temperatures.

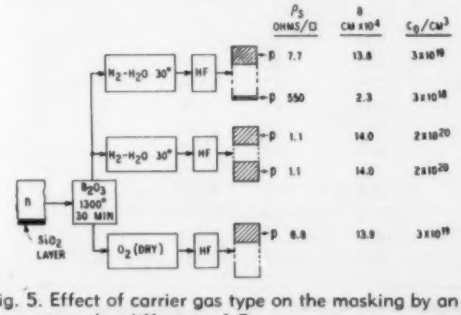

Fig. 5. Effect of carrier gas type on the masking by an oxide layer against the diffusion of B.

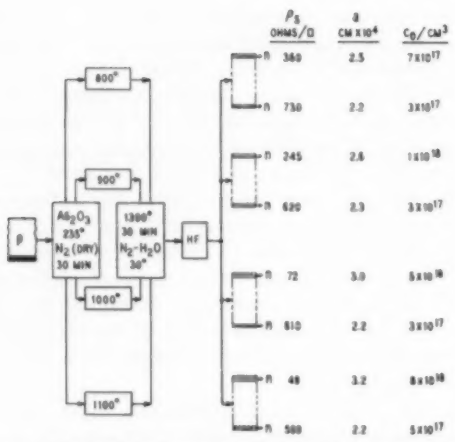

Fig. 6. Effect of predeposition temperature on masking and surface concentration.

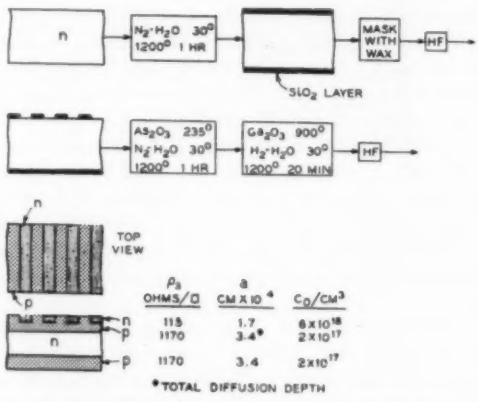

Fig. 7. Simultaneous production of single and double diffused layers of controlled structure by selective masking.

into Si at high temperatures should be very useful in the design of semiconductor devices. A few experimental results for wet hydrogen and nitrogen as well as oxygen are summarized in Table I.

Predeposition of Impurities

When a SiO_2 layer masks against the diffusion of an impurity, the simultaneous oxidation and addition of such an impurity may cause a partial masking effect on the unoxidized surface. Fig. 6 illustrates a technique for avoiding oxidation effects during the addition of the impurity. It consists essentially of predepositing the impurity in nonoxidizing gases such as N_2, He, or H_2 at low temperatures and for very short times. Under these processing conditions surface erosion is not appreciable. The diffusion of the impurity into the Si then may be carried out at higher temperatures and for longer times in oxidizing carrier gases.

In Fig. 6 As_2O_3 was predeposited for 30 min in dry nitrogen at 800°, 900°, 1000°, and 1100°C, respectively. The samples then were diffused for 30 min at 1300°C in N_2 bubbled through water at 30°C. The samples usually were washed in HF after the predeposition to remove any soluble deposits of the diffusant on the unoxidized surface and the preoxidized layer which now may contain some of the diffusant. This washing procedure was found to give more reproducible results.

As shown by the data in Fig. 6 the SiO_2 layer masks against the diffusion of As in the case of all four predeposition temperatures. The degree of masking, which is defined as the ratio of the surface concentration of the unoxidized surface to that of the oxidized surface, increases with predeposition temperature over the range studied. The data for the unoxidized surfaces also illustrate the usefulness of the predeposition technique for controlling the surface concentration over wide limits. The applica-

Table I. Masking by oxide surface layers against the diffusion of some donors and acceptors*

Diffusant Type	Diffusant Temp, °C	Diffusion Time, min	Diffusion Temp, °C	Surface type O	Surface type U	ρ_s (ohms/□) O	ρ_s (ohms/□) U	a (cm × 10⁴) O	a (cm × 10⁴) U	C_0/cm³ O	C_0/cm³ U
					N_2-H_2O-30°C Carrier gas						
As_2O_3	235	180	1100	P	N	—	340	—	0.7	—	5×10^{18}
As_2O_3	235	60	1200	N	N	3650	130	0.4	1.5	3×10^{17}	7×10^{17}
As_2O_3	235	30	1300	N	N	680	160	2.1	3.6	3×10^{17}	1×10^{18}
B_2O_3	1250	30	1250	N	P	—	76	—	5.1	—	7×10^{18}
B_2O_3	1300	30	1300	P	P	550	7.7	2.3	13.8	3×10^{18}	3×10^{19}
P (Red)	220	180	1100	N	N	2560	195	0.5	2.4	4×10^{17}	1×10^{18}
P (Red)	220	30	1300	N	N	885	170	3.6	7.4	8×10^{18}	4×10^{17}
Sb_2O_4	900	30	1300	N	N	1370	140	1.0	4.9	3×10^{17}	6×10^{17}
					H_2-H_2O-30°C Carrier gas						
As_2O_3	235	60	1200	P-N	N	—	330	—	1.3	—	1×10^{18}
As_2O_3	235	30	1300	N	N	680	86	2.1	3.7	3×10^{17}	2×10^{18}
B_2O_3	1300	30	1300	P	P	1.1	1.1	14.0	14.0	2×10^{20}	2×10^{20}
P (Red)	220	30	1300	N	N	745	150	3.6	5.6	1×10^{17}	4×10^{17}
Ga_2O_3	900	40	1200	P	P	1890	1835	5.8	5.8	6×10^{16}	6×10^{16}
Ga_2O_3	900	30	1300	P	P	675	675	9.1	9.1	1×10^{17}	1×10^{17}
Sb_2O_4	900	30	1300	P	N	—	160	—	5.6	—	4×10^{17}
					Dry O_2 carrier gas						
As_2O_3	235	30	1300	N	N	545	235	2.0	3.1	3×10^{17}	5×10^{17}
B_2O_3	1300	30	1300	N	P	—	6.8	—	13.9	—	3×10^{19}
P_2O_5	220	180	1100	N	N	1390	25	0.9	3.8	3×10^{17}	7×10^{18}
P_2O_5	220	30	1300	N	N	0.45	0.44	19.1	20.1	3×10^{20}	3×10^{20}

* Original samples about 5 ohm cm, preoxidized 1 hr at 1200°C in N_2-H_2O-30°C, U-oxide layer removed from this surface with HF before diffusions. O-oxide layer on this surface before diffusions.

tion of this technique for producing both *np* and *pn* double diffused layers from the same donor and acceptor impurity will be described later.

Multiple Layer Structures

A more interesting example of selective masking by a SiO_2 layer is illustrated in Fig. 7. After the preoxidation of an *n*-type Si sample in wet nitrogen at 1200°C, the oxide layer is removed from one surface to give alternate oxidized and unoxidized bands. This is done by applying alternate bands of wax, washing in concentrated HF, and then removing the wax with a solvent. An As diffusion followed by a Ga diffusion and an HF wash results in the structure illustrated by the top and cross-section views shown in the bottom left of Fig. 7. Note the alternate *p*- and *n*-type surfaces as well as the alternate single and double diffused layers. These correspond to the alternate oxidized and unoxidized bands, respectively, on the top face before the diffusion operations. The bottom surface, which is completely covered with an oxide layer before the diffusion treatments, is entirely *p*-type with a single diffused layer. A similar structure results if Sb_2O_3 heated at 900°C is substituted for the arsenic trioxide.

It is not necessary to remove the oxide layer after the As diffusion since Ga is not masked by the SiO_2 layer under these processing conditions (see Table I). Actually the oxide layers covering the *n*- and *p*-type surfaces before the final HF wash are distinctly different in color. The color difference probably is due to a thickness difference between the two oxide layers. This is indicated since the same colors are observed when the identical heating sequence is employed without the addition of the As and Ga. The color difference of the oxide layers covering the *n*- and *p*-type Si surface areas is useful in device fabrication as an aid in locating these regions after diffusion.

A transistor (6) has been made by these techniques which had an alpha of 0.91 at a collector voltage of 10 v and an emitter current of 1 ma. The unique feature of this transistor structure was the ability to make a direct contact on the same surface to both the diffused base layer and the diffused emitter layer. In previously described double diffused transistors (3), the base contact was made by alloying Al through the emitter layer. The direct contact to the base layer described in this paper also should allow a higher surface concentration in the emitter than is permissible in the Al alloy base contact structure.

The structure obtained in Fig. 7 can best be explained by referring to Fig. 8. This illustrates the appreciably lower surface concentration of As in the oxidized surface as compared to the unoxidized surface. Since the Ga is not masked by the SiO_2 layer under these processing conditions, its surface concentration is equivalent for both surfaces. Thus the As overdopes the Ga on the unoxidized surface, while the reverse is true on the oxidized surface. In other words a *np* diffused structure is produced in the unoxidized surface and a single *p* diffused layer is produced in the preoxidized surface. The surface concentration of the diffused As layer in the oxidized

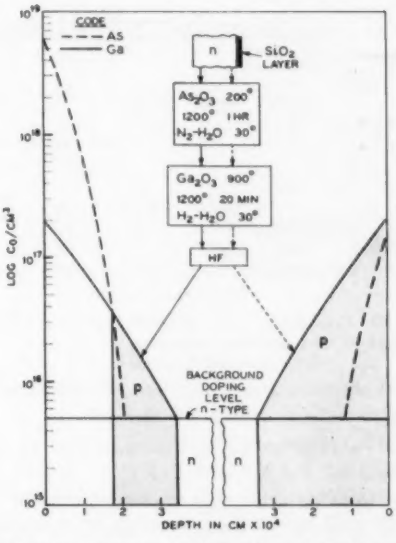

Fig. 8. Plot to illustrate the formation of single and double diffused layers by selective masking.

surface was not determined in this experiment and is drawn merely for illustration.

Fig. 9 shows a photograph of an actual diffused structure which was produced by the selective masking technique just described. The diffused layers on one surface were exposed by lapping at a 5 degree angle (5) perpendicular to alternate *p*- and *n*-type surface bands similar to those illustrated in Fig. 7. The *p* region was darkened by the HF-HNO_3 staining technique (5). Note the single *p* diffused layer in the center region with double *np* diffused layers on either side. While not evident from the photograph, the dark surface or *p* region indexes very closely with the original preoxidized surface.

Controlled structures with either *n*- or *p*-type single diffused layers and either *np*- or *pn*-type double diffused layers have been produced by the selective masking procedure when the proper diffusants and processing conditions are employed. Moreover, both structural types have been produced with B and P by employing the predeposition technique. This combination of impurities also can be employed for producing low resistance surface layers for collector contacts in transistor construction. The essential processing steps for producing either an *np*-

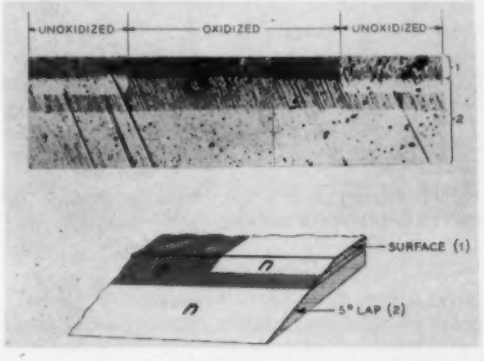

Fig. 9. Photograph of single and double diffused layers produced by selective masking.

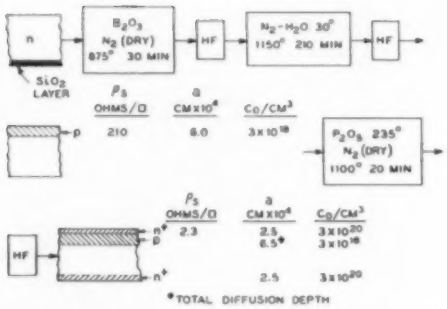

Fig. 10. Production of a p^+pnn^+ transistor structure by predisposition and selective masking.

or *pn*-type transistor structure of this type with B and P are shown in Fig. 10 and 11.

In the *np* structure illustrated in Fig. 10, the predeposition of the B_2O_3 at 875°C in dry N_2 gives a surface concentration (C_0) on the unoxidized surface which is well below that eventually reached by the P. The processing conditions are chosen to give the desired final diffusion depth of the *p*-layer into the originally unoxidized surface. Because of the masking effect of the oxide layer during the predeposition of the boron trioxide, the C_0 of the oxidized surface is reduced to well below that of the unoxidized surface. Actually no B conversion layer is formed in the oxidized surface under these processing conditions. Thus the structure illustrated by the last cross section in Fig. 10 results after the final phosphorus diffusion.

The *pn* structure illustrated in Fig. 11 is produced in a similar manner except that the P is masked and its surface concentration is reduced by predeposition below that eventually reached by the B. In this case a conversion layer is formed in the oxidized surface by the P. However, the partial masking by the oxide layer is sufficient to reduce the diffusion depth below that finally attained by the B layer. Because of this only a p^+ layer is formed on the original oxidized surface as shown in Fig. 11. At these low doping levels, red P as a source of P vapor gives more reproducible results than P_2O_5. Red P also generally results in lower surface concentrations than the phosphorus oxide for otherwise similar processing conditions.

In addition to the structural possibilities of masking, it also can be applied in conjunction with the

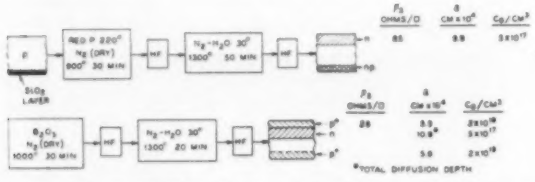

Fig. 11. Production of p^+npp^+ transistor structure by predeposition and selective masking.

predeposition technique to provide a wide range of controlled impurity levels in diffused layers. For example, by modifying the processing conditions illustrated in Fig. 10 and 11, the doping levels of the base and emitter layers can be varied over wide limits.

It is evident from the few examples of selective masking described that a large variety of structures can be produced by the proper choice of processing conditions. It is hoped that the examples given illustrate the essential procedures for producing such structures.

Summary

The use of oxidizing atmospheres has been shown to provide surface protection of Si surfaces during high temperature heating operations. The protection results from the enclosure of the Si in a SiO_2 envelope. The latter also provides a means for masking against the diffusion of some impurities into Si at high temperatures. The masking effectiveness of the oxide layer is determined by several process parameters such as time, temperature, carrier gas composition, impurity type, impurity compound, and preoxidizing conditions. Thus far, processing parameters have been established for masking B, As, Sb, and P. Precise surface structures of both *n*- and *p*-type as well as the simultaneous production of single and multidiffused junction layers are possible by this masking technique. Finally, a wide range of controlled impurity levels in diffused layers can be obtained by means of a new predeposition technique.

Acknowledgment

The authors wish to thank several people for their contribution to this investigation. In particular, the authors are grateful to C. S. Fuller, M. Tanenbaum, J. L. Moll, and F. M. Smits for their helpful discussions; to G. Backenstoss for the calculations of the surface concentration values; and to H. E. Bridgers for supplying the crystal ingots. Thanks also are due to R. M. LeBach for some of the measurements.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1958 JOURNAL.

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Density and Viscosity of Titanium Tetrabromide

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ABSTRACT

Measurements were made of the density and viscosity of liquid $TiBr_4$. Measurements of the vapor density at the boiling point indicate that $TiBr_4$ is monomolecular.

Because of widespread interest in Ti as a strong, light-weight, corrosion-resistant construction material, many and formidable research efforts are being directed toward the development of low-cost processes for production of the metal from its relatively abundant ores. However, since the literature on the compounds of Ti is incomplete, progress would be enhanced by determination of reliable values for some of the physical and thermodynamic properties of Ti halides. These compounds represent potential intermediates in the extractive metallurgy of Ti.

The present work is part of an effort directed toward establishing the physical and thermodynamic properties of titanium bromides. The vapor pressure and thermal properties of $TiBr_4$ are the subject of another paper to be published soon.

Preparation of $TiBr_4$

$TiBr_4$ was prepared by direct synthesis from "iodide" Ti [2] and distilled Br.[3] In a typical preparation, 1 lb Br was placed in a 500 ml Pyrex flask provided with a water-cooled reflux condenser and a 9 mm sealed side arm for later use in transferring the product. After the Br had been heated with a mantle to 58°C, degreased HF-washed and dried turnings of Ti were added through the condenser under a blanket of argon which had been purified by passing through Ti chips at 1000°C. The turnings ignited spontaneously on contact with the liquid Br. A 3 in. diameter ring of Vycor extending above the Br surface acted as a fence to prevent burning pieces of Ti from contacting and cracking the Pyrex reaction flask. The burning Ti had no apparent effect on the Vycor.

The rate of addition of Ti chips was governed by the rate at which the heat of reaction could be dissipated. After approximately ¾ of the stoichiometric quantity of Ti had been added, some of the turnings settled to the bottom without reacting. The rate of reaction tapered off until it was finally necessary to supply heat to boil the liquid. Invariably some free Br remained.

One of two techniques, atmospheric and vacuum distillation, was used to purify the crude bromide.

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[2] Prepared at Battelle by the thermal decomposition of titanium tetraiodide (1).

[3] Mallinckrodt Chemical Works, St. Louis, Mo.

Table I. Analysis of $TiBr_4$

Sample	% Ti		% Br	
	Found	Formula	Found	Formula
A	13.1	13.03	—	86.97
B	13.2	13.03	86.8	86.97
C	—	13.03	87.0	86.97

Spectrographic Analysis of the Hydrolysis Product of Sample C

	%		%
Ti	Major		
Si	<0.002	Sn	<0.0005
Fe	<0.001	Ni	<0.0003
Al	<0.001	Mo	<0.0005
Mn	0.003	V	<0.002
Mg	<0.001	Cd	<0.001
W	<0.010	Zn	<0.0015
Ba	<0.001	Zr	<0.001
As	<0.0025	Co	<0.0002
B	0.0008	Ca	<0.0005
Sb	<0.0005	Cr	<0.001
Pb	<0.0005		

Table I gives analyses of the $TiBr_4$ purified by distillation in a 30 plate column at atmospheric pressure. Ti was determined as TiO_2 and Br by the standard Volhard method.

Although the analyses given in Table I deviate from the formula values to a greater extent than would be desired, it is thought that this reflects limitations in the analytical technique, rather than variable purity.

Further evidence of the purity of the $TiBr_4$ used in this work is the reproducibility of vapor-pressure data taken with intermediate resublimation of samples in place. Freezing-point measurements indicate that the liquid-soluble, solid-insoluble impurity content is something less than 0.00008 mole fraction, which is negligible for the present purposes.

To avoid contamination, transfer of the $TiBr_4$ was accomplished through the use of Pyrex break seals either under vacuum or an atmosphere of purified argon.

Vapor Density

The vapor density of $TiBr_4$ was measured by the Dumas technique (2) suitably modified to avoid con-

Table II. Vapor Density of $TiBr_4$

Experiment	Bath temp, °C	Pressure, atm	Vol of flask, ml	Wt of $TiBr_4$, g	Mol wt
1	243.7	0.9783	250.5	2.1837	377.9
2	246.9	0.9794	246.8	2.0698	365.5
3	245.9	0.9793	253.7	2.1548	369.5
4	237.1	0.9746	250.7	2.0970	359.4
5	242.5	0.9776	253.4	2.1336	364.5
					Avg. 367.3 ± 6.2

tact of the $TiBr_4$ with air. Results are summarized in Table II.

Comparison of the average result, 367.3 ± 6.2, with the formula weight, 367.56, shows that $TiBr_4$ vapor is monomeric and undissociated at the boiling point.

Liquid Density

The density of liquid $TiBr_4$ was determined with a Mohr-Westphal balance (3). The displacement method was chosen over direct pycnometric measurement, since the technique of making measurements on the volatile, reactive $TiBr_4$ at elevated temperatures was greatly simplified. However, some sacrifice in accuracy resulted.

The $TiBr_4$ was contained in a cell continuously purged with dry He through the tube which enclosed the plummet suspension. The purge effectively prevented contamination of the sample resulting from the diffusion of air down the tube.[4] The reading of the balance was independent of the purge-gas flow rate over a wide range, indicating that the drag on the suspension wire was insignificant. It was necessary, however, to correct for the effect of surface tension on the suspension wire.

The volume of the plummet was determined by displacement in distilled water, C.P. CCl_4, and C.P. C_6H_6 at measured temperatures near room temperature. Density data for these liquids were taken from the International Critical Tables and checked with a pycnometer. After all corrections were made, the volume of the plummet as determined in the individual liquids differed from the average by ±0.3%, placing that much uncertainty on subsequent measurements of the density of $TiBr_4$.

Results given in Table III were obtained with two preparations of $TiBr_4$, as indicated. Temperature measurements were made with a calibrated Chromel-Alumel thermocouple and a semiprecision potentiometer. The temperature of the oil bath containing the cell was controlled to ±0.1°C.

It will be noted that the data may be expressed by the equation

$$d = 2.953 - 0.00225\ (t - 40) \qquad (I)$$

to within ±0.03%. This deviation would encompass temperature errors of up to ±0.5°C because of the low temperature coefficient. However, since the values are dependent on the uncertain calibration mentioned above, the over-all uncertainty is ±0.3%.

[4] After standing in the apparatus for three days, one sample became visibly contaminated with hydrolysis products, resulting in an apparent decrease in density of 0.2%.

Table III. Density of Liquid $TiBr_4$

Sample	Temp, t, °C	d, g/cc, obs.	d, g/cc, calc.[a]	d, calc.-obs.
A	42.4	2.947	2.948	+0.001
A	48.8	2.933	2.933	0.000
A	55.2	2.919	2.919	0.000
A	64.1	2.899	2.899	0.000
A	71.4	2.882	2.882	0.000
A	80.0	2.863	2.863	0.000
A	86.5	2.849	2.848	−0.001
A	91.9	2.837	2.836	−0.001
B	80.1	2.864	2.863	−0.001
B	87.6	2.846	2.846	0.000
B	98.1	2.822	2.822	0.000
B	105.6	2.805	2.805	0.000
B	113.2	2.788	2.788	0.000
B	118.6	2.776	2.776	0.000
B	122.2	2.769	2.768	−0.001

[a] Calculated from the equation, $d = 2.953 - 0.00225\ (t - 40)$.

Liquid Viscosity

The viscosity of liquid $TiBr_4$, prepared and purified as described earlier, was measured by means of an Ostwald viscometer (4) into which the sample was sealed under its own vapor pressure. The viscometer, contained in an oil bath with ±0.1° temperature control, was calibrated with ethyl alcohol and CCl_4. Viscosity and density values for the reference liquids were taken from the International Critical Tables. The density of $TiBr_4$ was taken from the preceding work. The standard deviation in the values obtained for the viscometer constant was ±1.2%.

A single sample of $TiBr_4$ was used to obtain the data given in Table IV and Fig. 1 which may be expressed to ±0.36% in η by the equation

$$\mathrm{Log}_{10}\eta = 102{,}310/T^2 - 177.12/T - 0.1947 \qquad (T \text{ in } °K) \qquad (II)$$

The ±0.3% scatter in the data would encompass temperature errors in the middle of the range of as much as ±0.5°C, which is outside the estimated

Table IV. Viscosity of Liquid $TiBr_4$[a]

Temp, °C	η obs., centipoise
42.2	1.880
51.9	1.702
62.1	1.551
79.4	1.341
87.9	1.254
95.0	1.198
99.3	1.170
118.0	1.052
127.1	1.001
112.4	1.086
102.9	1.138
92.5	1.217
82.0	1.313
74.0	1.392
65.0	1.502
54.1	1.657
52.8	1.672
43.4	1.836
59.6	1.567
68.2	1.457
68.6	1.457
99.7	1.161

[a] Data listed in the order taken.

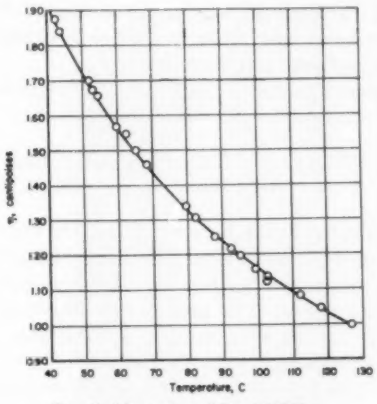

Fig. 1. Viscosity of liquid $TiBr_4$

error (±0.2°C) of the temperature measurements. The 0.3% uncertainty in the density measurements is of the same order as the above scatter. Therefore, the limiting factor in the validity of the viscosity results is the 1.2% uncertainty in the calibration of the viscometer.

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Electrolytic Preparation of Titanium from Fused Salts

I. Preliminary Electrolytic Studies with Diaphragmed Cells

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ABSTRACT

Reduced titanium chlorides dissolved in fused alkali and alkaline earth chlorides may be electrolyzed in diaphragmed cells under an inert gas atmosphere to yield ductile titanium as adherent, crystalline deposits. The reduced titanium chlorides are prepared *in situ* by adding $TiCl_4$ through a hollow cathode at a controlled feed to current ratio.

Interest has been centered in recent years on the development of an electrolytic Ti metal process in order to avoid the difficult and batchwise operations of present commercial processes based on the reaction of $TiCl_4$ with an active reducing metal, such as Mg or Na.

The electrolysis of reduced titanium chlorides in fused salt baths has recently been described by others (1-7). In addition, a number of patents (8-13) have been issued. Review articles (5, 14) on the electrodeposition of Ti metal have been published.

In this paper experiments on the fused salt electrolytic reduction of $TiCl_4$ to the lower chlorides, $TiCl_3$ and $TiCl_2$, and further reduction to Ti metal are described. This information has served as a basis for further development in three directions, a stepwise reduction of $TiCl_4$ to Ti metal, a one step reduction of $TiCl_4$ to metal, and an electrorefining process.

At the inception of this program very little information was available on such properties of the reduced titanium chlorides as their solubility in fused salt systems, their stability, and their position in the electrochemical series. It appeared reasonable from the known ability of Mg to reduce $TiCl_4$ directly to metal that either Mg or any cations which required higher deposition potentials would be compatible with Ti deposition, but other common cations could be expected to deposit with or prior to Ti. Data here on deposition of Ti and recent free energy data (15) support these limitations. Since Ti is highly reactive with oxygen-containing compounds, the melts were also limited to anions not containing oxygen; the chlorides were most convenient. The ease of oxidation of the reduced titanium chlorides required that the melts containing them be maintained under an inert atmosphere. In addition, contact of the reduced titanium chlorides with an oxidizing anode, specifically an anode producing Cl_2, had to be avoided if a substantial portion of the dissolved Ti were not to be reoxidized and ultimately lost from the system as $TiCl_4$. This required the use of a porous diaphragm. A gas barrier was desirable to prevent Cl_2 produced at the anode from contacting the reduced titanium chloride melts and also any metal cell parts.

Experimental

Equipment.—A number of laboratory cells were designed ranging in size from 0.4 to 10 l melt capacity. A typical cell of approximately 10 l capacity is shown in Fig. 1. The cell itself was of fused silica

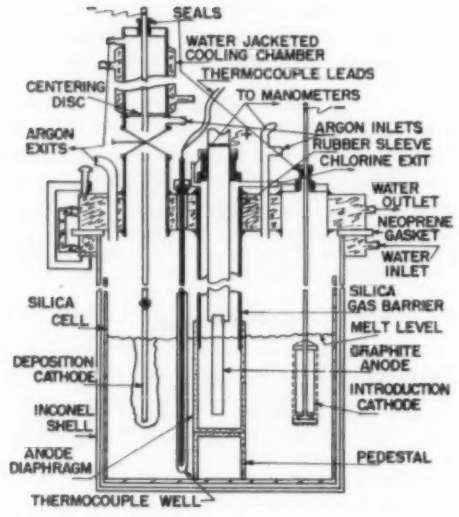

Fig. 1. Schematic drawing of electrolytic cell for Ti deposition.

contained within an Inconel outer shell and externally heated in a Globar furnace. The use of a water cooled flange and cell top permitted the cell to be tightly sealed. The diaphragm was a porous alumina cylinder (Norton Co., Alundum, grades RA98 or RA1139) resting on an alumina pedestal and loosely fitted with an internal fused silica sleeve that served as a gas barrier. Cathodes were of Ni and the anodes were graphite. The cell was carefully pressure checked after assembly and also at intervals throughout a run to insure that it was leaktight. Argon for the cell atmosphere was high purity commercial material further gettered by passage over Ti metal chips at 800°C. A cell such as that illustrated had a continuous, useful life in excess of three months.

Preparation of reduced titanium chloride containing melts.—For initial electrodeposition experiments a $TiCl_3$-LiCl mixture was prepared by reacting stoichiometric amounts of $TiCl_4$ with molten Li dispersed in mineral oil. The resulting product was washed free of mineral oil with CCl_4, and dried. Although the material did not react too rapidly with air, the electrodeposited metal was badly contaminated with oxides. The electrowinning of Ti metal through the use of such a reduced titanium chloride preparation might be considered as only three-quarters electrolytic, because of the reduction of $TiCl_4$ to $TiCl_3$ by chemical means.

For these reasons consideration was given to the preparation of reduced titanium chlorides directly in the catholyte. A suitable procedure was found to be the introduction of $TiCl_4$ underneath the surface of the melt in juxtaposition to a cathode which was passing current at the rate of from one to about two faradays per mole of $TiCl_4$. Under these conditions practically all the $TiCl_4$ was solubilized as $TiCl_3$ or $TiCl_2$, respectively. It was convenient to use a hollow tubular cathode through which the $TiCl_4$ was introduced as vapor or directly as liquid which vaporized as it approached the melt level. A stream of inert carrier gas was used with low $TiCl_4$ flow rates to keep salt melt from being drawn up the tubular cathode and freezing.

It appears that the $TiCl_4$ is solubilized chemically. During most of the introduction stage the reaction is

$$TiCl_4(\text{gas}) + TiCl_2(\text{solution in melt}) \rightarrow 2TiCl_3(\text{solution in melt})$$

with the cathode reaction being largely the reduction of trivalent Ti to divalent Ti. Supporting this viewpoint is evidence showing $TiCl_4$ to be soluble in Ti^{3+}-containing melts. The measured cathode potentials, generally 1.8-2.0 v vs. a Cl_2 electrode, are consistent with the proposed cathode reaction.

It has also been possible to prepare reduced titanium chlorides in the catholyte by reacting $TiCl_4$ with a bed of Ti metal, either scrap or metal dropped from a cathode. In cells for the electrorefining of Ti metal the hollow cathode device has been combined with the use of a scrap Ti anode, so that a portion of the reduced titanium chlorides of the bath derives from the $TiCl_4$ introduced through the hollow cathode and the remainder from the scrap Ti anode (16).

Experimental Procedure

For several of the salt systems studied the salt bath was obtained simply by fusing the reagent grade, predried components in the cell under an argon atmosphere. In some cases, particularly LiCl- or $MgCl_2$-containing systems, the fused salts were found to contain considerable quantities of moisture; it was necessary to getter the melt by reacting with Ti metal chips and then filtering under argon through a porous alumina filter directly into the cell. In the case of readily hydrolyzable salts, particularly $CaCl_2$- and $MgCl_2$-containing melts, NH_4Cl was added during fusion to prevent hydrolysis and oxide formation.

In a typical run, after the salt was fused, $TiCl_4$ was added through the hollow cathode at a rate of one mole for two faradays, the rate being maintained by a flowmeter and buret system. The cathode current density was approximately 0.2 amp/cm^2, or 50 amp in the cell of Fig. 1. After the Ti concentration had been brought to the desired level, a slow reduction period at about 0.1 amp/cm^2, total current 25 amp, could be interposed to improve the degree of reduction of the melt. This was not generally required for the cell illustrated. The deposition cathode was placed in the closed withdrawal chamber, flushed with argon for 15 min and then lowered into the cell. A 100 amp-hr deposit was taken at 1.0 amp/cm^2, or a total current of 50 amp. Successive deposits were taken until the Ti concentration of the melt was below about 0.1*M* as marked by a fairly sharp increase in cell emf. The $TiCl_4$ charging cycle was then resumed. Deposits adhered to the cathode quite well as long as the melts were free of water and other contaminants. A typical deposit is shown in Fig. 2. The metal, after being leached with 1% HCl to dissolve the occluded salts, was easily removed from the cathode, washed further with water, and dried at 110°C. The Cl_2 produced at the anode was measured and vented to the air. Over-all cath-

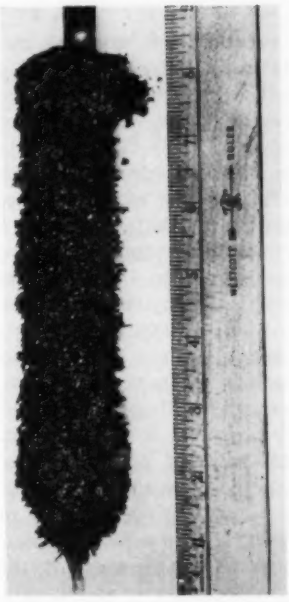

Fig. 2. Electrolytic deposit of Ti

ode and anode current efficiencies were generally in the range of 80-90%.

Samples of the melt were obtained either by drawing the liquid up thin glass tubes where freezing occurred rapidly or by introducing a small silica sampling tube fastened to a cathode. Melts were analyzed for total Ti (expressed on a molal basis, that is moles of Ti/kg of diluent salt) by a volumetric ferric ammonium sulfate titration and for degree of reduction either by titrating the acid liberated on oxidation and hydrolysis of the sample or by measuring the volume of hydrogen liberated on dissolving the divalent Ti-containing samples in dilute acid. The degree of reduction was expressed by an N value, representing the apparent valence of the Ti in the melt, viz., the subscript in the empirical formula $TiCl_N$ for the titanium chlorides present. Thus N would be 2 if the Ti were entirely divalent, 3 if the Ti were entirely trivalent.

Fig. 3. Photomicrograph of Ti metal

Parameters in Metal Deposition

Degree of melt reduction.—Experimentally it was found that one of the most important factors affecting the nature and quality of the deposits was the degree of reduction of the melt. Generally, as the N value decreased toward the equilibrium value set by the reaction

$$Ti + 2TiCl_3 \rightleftharpoons 3TiCl_2$$

the crystal size and purity of the metal showed a marked increase. The equilibrium N value was found to be 2.0 for LiCl-KCl melts at 400°-500°C, and 2.15 for NaCl or $SrCl_2$-NaCl melts at 700°-900°C for concentrations of the order of 1M. If serious air leakage occurred during $TiCl_4$ introduction, the N value was above 2.5. Deposits obtained from these melts were finely crystalline, most of the metal being less than 100 mesh and including as much as 90% by weight of fused salt. In this case the melt was further reduced by passing current at 0.1-0.2 amp/cm^2. Under these circumstances the dominant reaction was the reduction of trivalent to divalent Ti. Higher current densities polarized the trivalent to divalent Ti reaction and resulted in the formation of metal deposits. When the N value was reduced to approximately 2.3, the metal obtained was coarsely crystalline and mostly greater than 100 mesh in size. Occluded salts ranged from 10 to 50% based on total deposit weight. A photomicrograph of the product is shown in Fig. 3. This product could be handled readily after leaching either by pressing and hot sintering or by fusion in a water-cooled copper arc furnace.

While the reason for this increase in crystal size is not certain, it is suggested that, as melt reduction is improved, the melt becomes less contaminated with soluble impurities that could interfere with crystal growth. For example, a melt reduced to the equilibrium condition could not contain, in principle, any soluble impurities capable of reacting with Ti metal itself to form an insoluble phase. Removal of these impurities permits the growth of larger crystals and results in improved purity for the crystal grown.

Melt composition.—Deposition of adherent, coarsely crystalline metal has been accomplished successfully in various melts containing all the alkali and alkaline earth cations including Mg. Certain melts are less desirable because of hygroscopicity, excessive tendency toward hydrolysis or oxidation, or higher melting point. The $SrCl_2$-NaCl eutectic system, containing 73% $SrCl_2$, mp 565°C (17), was found to be particularly suitable. Typical operating temperatures were in the range 650°-750°C. It appears that the presence of Sr ion allows some improvement in metal crystal size. Thus, a product containing less than 1% minus 100 mesh was readily prepared. Coarsely crystalline deposits were also prepared in bromide and iodide baths containing the corresponding reduced titanium halides, but these baths offered no advantage over the chloride baths.

Cell sealing.—One of the most important factors in electrolytic cell operation was found to be the degree to which sealing of the equipment had been

accomplished. Oxygen and nitrogen contamination of the cell atmosphere interfered with extended operation by forming a sludge layer which ultimately short-circuited the cell, by oxidizing the soluble Ti in the melt making it difficult to obtain well reduced melts, by seriously decreasing yields, and finally by directly causing some reduction in deposit purity. In well sealed cells, metal with a hardness less than 110 Bhn was obtained consistently.

Temperature.—The effect of temperature on the product was less important. Temperatures of 400°-500°C with the LiCl-KCl bath resulted in finer crystals with the crystal faces somewhat rounded. Increased temperature resulted in larger crystal size. The change in phase of Ti at 885°C, as observed in a NaCl bath, was reflected in a change in the shape of the individual crystals, but the generally dendritic nature of the deposits was retained. Deposits were obtained at temperatures in excess of 1000°C, but no advantage was gained by operation at this temperature and cell life was shortened.

Melt agitation.—Stirring during metal deposition by use of a rotating cathode or by bubbling argon through the melt was found to reduce markedly the crystal size of the metal being deposited. In addition, agitation could disturb any oxygen containing sludge resting on the cell bottom and further contaminate the deposit.

Soluble titanium concentration.—Electrolysis was usually performed at Ti concentrations between 0.1 an 1*M*, although deposits were also obtained beyond this range. Below 0.2 *M* at about 1 amp/cm^2 for the $SrCl_2$-NaCl melt at 700°C and below 0.1*M* for the NaCl melt at 850°C, metal deposits became spongy adjacent to the cathode, apparently representing the effects of polarization. Aside from this, the effects of Ti concentration were very minor in the range covered. From a practical point of view it is preferable to operate at lower concentration to minimize losses of soluble Ti by salt dragout and diffusion through the diaphragm. For example, it was found difficult to bring the catholyte concentration above 4*M* because of increasing losses through the diaphragm.

Cell electromotive forces.—Difficulty was experienced in measuring accurately the emf's of diaphragmed cells because of the tendency of reduced Ti melts to lay down conductive layers of reduced Ti compounds (18) or sludge, thereby introducing a spurious bipolar emf at the diaphragm that became more pronounced as a cell became older. At low operating currents, reduced titanium chlorides which diffused through the diaphragm depolarized the Cl_2 electrode. This was partly overcome by providing a separate chlorine measuring electrode fabricated from a porous carbon plug. The potential for the cathodic reduction of trivalent to divalent Ti was particularly difficult to measure because the reaction was apparently polarized up to the potential for the deposition of Ti at relatively low current densities. Also the metals used for the measuring electrode became titanized (19). Therefore their inertness is open to question. A value of 1.85 v is representative of the reaction

$$TiCl_3 \rightarrow TiCl_2 + \tfrac{1}{2}\, Cl_2(gas)$$

when both reduced salts are at a concentration of 0.5*M* in a $SrCl_2$-NaCl bath at 700°C. The cell emf for the reduction to metal and Cl_2 of a 1*M* reduced titanium chloride bath, close to the equilibrium value (*N* value of 2.15) is 2.05 v. As the total Ti concentration approached zero, the value of the cell emf rose sharply to 3.3 v which is the expected value for the deposition of alkali metal and chlorine (15).

Cathode current density.—The nature of the deposit has not proved to be a marked function of cathode current density under normal deposition conditions. At very low current densities most of the current is used to reduce trivalent to divalent Ti, unless the bath is substantially in equilibrium with Ti metal. Under normal operating conditions, therefore, little or no metal is deposited at the cathode. In general, for baths of moderate Ti concentrations, crystal size increased slightly with increasing current density; 1 amp/cm^2 was usually near optimum.

Anode current density.—Difficulties with excessive anode current densities usually have been due to secondary effects, such as plugging anode gas outlets with salt spray. In cells having a very low Ti concentration a sudden rise in resistance between anode and melt, usually characterized as an anode effect, was observed with the $BaCl_2$-NaCl eutectic bath at anode current densities above 1 amp/cm^2 and other baths at somewhat higher current densities. However, once charging of the bath has been started, the evolution of a small amount of $TiCl_4$ from the anode seems to avoid the effect at practical anode current densities.

Ionic migration effects.—Since considerable quantities of charge were being carried through these cells, ionic mobility effects could be expected. With the porosity and pore size of alumina employed for diaphragms in this work the effect was substantially undetectable, although measurements of the catholyte and anolyte melt depth have indicated that the latter stood a little lower during cell operation. With finer porosity diaphragms, for example Norton Alundum grade RA360, the effect was more marked and, in extreme cases, the anolyte melt level lowered to such an extent that contact with the anode was broken. These findings indicate that a very large fraction of the current is carried by the cations. Experiments in which the cathode was surrounded by a second diaphragm indicated that most of the current was carried not by the Ti but by the other cations of the bath, at least for melts of Ti concentration less than 1*M*.

Summary

A process has been developed for the electrolytic conversion of $TiCl_4$ to metal and chlorine which involves the reduction of $TiCl_4$ to a reduced titanium chloride in solution in an alkali or alkaline earth chloride mixture for which the over-all reaction is formally

$$TiCl_4 \xrightarrow{4\text{-}N \text{ faradays}} TiCl_N + \frac{4\text{-}N}{2}\, Cl_2$$

The resulting reduced titanium chlorides were then reduced further to Ti metal

$$TiCl_x \xrightarrow{N \text{ faradays}} Ti + \frac{N}{2} Cl_2$$

By controlling the melts for the deposition of metal so that most of the dissolved Ti was in the divalent condition and by protecting the reduced titanium chloride-containing melts with an inert atmosphere it was possible to obtain Ti metal as a coarsely crystalline dendritic material, sufficiently adherent to the cathode to permit its removal from the cell. The deposits after being leached with dilute HCl were readily fabricated into ductile Ti metal pieces either by arc melting or powder metallurgical means. Since the melt after the completion of a cycle of electrolysis was substantially the same as the initial melt, the process has the elements necessary for continuous or semi-continuous operation on a larger scale.

Data have been obtained against a chlorine electrode for the emf's corresponding to the two major cathode reactions being carried out in the cell, viz., the reduction of trivalent to divalent Ti and the reduction of an equilibrium mixture of divalent and trivalent Ti to Ti metal.

Information has also been presented on the other parameters of the electrolysis such as the influence of temperature, current density, and melt composition.

Acknowledgment

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Electrochemical Polarization

II. Ferrous-Ferric Electrode Kinetics on Stainless Steel

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ABSTRACT

The oxidation-reduction kinetics of the ferrous-ferric sulfate system have been measured on a stainless steel surface. The data completely support theoretical equations which describe the potential-current relationships for such a system. The analysis applies to reversible electrodes and to corroding electrodes where the potential is determined by two intersecting activation overvoltage functions. Also, the analysis permits calculation of a number of electrochemical constants with a minimum number of experimental observations. The possibility of determining anode-to-cathode area ratios for corroding metals is discussed.

One of the most important trends in recent studies of electrochemical kinetics consists of the development of equations which describe the potential current relationships of an electrode (1). Bockris (2) has described these relationships in great detail, primarily for electrodes which exhibit the reversible potential. Stern and Geary (3) have extended these concepts to include electrodes at which more than one oxidation-reduction system is operative. An understanding of the nature and shape of polarization curves is important in practical studies of corrosion phenomena, electrodeposition, and battery performance.

The equations illustrated by Bockris are derived entirely from kinetic theory. Although different investigations support various phases of the theory, no

one study has been conducted which attempts to verify directly the entire concept. The equations should permit calculation of the Tafel constants for anodic polarization from cathodic measurements alone. Also, low current measurements are related to the anodic and cathodic Tafel constants.

This discussion considers experimental observations of the electrode kinetics of the ferrous-ferric oxidation-reduction systems in the light of this theory.

Apparatus and Procedures

The cell used for polarization measurements was similar to that described elsewhere (4) except that a Luggin capillary probe was not necessary because of the extremely low currents entailed in the measurements. Platinized Pt was used as a reference electrode and as auxiliary electrodes during anodic and cathodic measurements. Linde prepurified nitrogen gas was bubbled through the cell at all times.

Solutions were prepared from reagent-grade chemicals and distilled water. The material studied was commercial Type 304 stainless steel, annealed at 1050°C for 1 hr and water-quenched. The steel contained 18.36% Cr, 9.06% Ni, 0.94% Mn, and 0.05% C. The surface was degreased in boiling acetone and benzene, immersed in concentrated HCl until hydrogen evolution was observed, thoroughly rinsed in distilled water, washed in concentrated HNO_3, rinsed again, and immersed directly into the cell.

Potential measurements were made using a L&N pH meter as a high-impedance galvanometer in series with a precision Rubicon potentiometer. This system permits potential measurement to ±0.2 mv. The sensitivity was increased where necessary by feeding the output signal from the pH meter into a 0- to 1-mv recorder which was then used as the null detecting device. Applied current values below 10^{-7} amp were measured with an electrometer and a precision 10-megohm resistance. Values between 10^{-7} amp and 10^{-6} amp were measured by determining the *IR* drop across 0.1 and 0.01 megohm standard resistances. Higher current values were determined directly with a precision Weston microammeter.

Results

One of the more serious problems in activation polarization measurements arises from interference due to resistance and concentration polarization. This usually occurs because the exchange current, i_o, for most practical reversible electrodes is so high that considerable current must be applied in order to polarize the surface. Thus, the use of a Pt surface to study ferric-ferrous oxidation-reduction kinetics creates difficult experimental problems. An ideal surface for use in comparing experimental observations of electrochemical polarization with theory requires a material which does not corrode[1] and which exhibits a low exchange current. Stainless steel in a solution of ferric and ferrous sulfate is a suitable system for such a study.

[1] Actually the surface may react with the environment slightly, as long as the corrosion current is several orders of magnitude lower than the exchange current. Under these conditions, the electrode will still exhibit the equilibrium potential and will behave ideally.

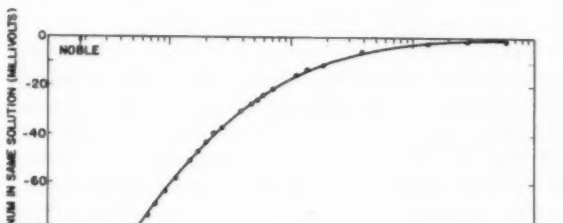

Fig. 1. Potential as a function of time for Type 304 stainless steel immersed in ferric-ferrous sulfate.

The solution was prepared by adding 100 g of $(Fe)_2(SO_4)_3 \cdot 9H_2O$ and 0.7 g of $FeSO_4 \cdot 7H_2O$ to 1 liter of water. The equilibrium ferric-ferrous potential of a solution prepared in this manner and measured with a platinized Pt electrode is approximately 0.770 v on the standard hydrogen scale. The equilibrium potential of such a solution is not exactly reproducible from batch to batch because the ferrous salt contains varying amounts of ferric contamination.

Potential-Time Behavior

When an electrode is prepared as described above, the initial potential is active to Pt in the same solution but slowly approaches the ferrous-ferric potential on Pt. A steady-state value of 1 mv more active than the reversible ferric-ferrous potential is achieved after about 100 hr. Fig. 1 illustrates this initial time dependence.

Polarization

Theory.—For an electrode at equilibrium, the rate of oxidation of ferrous ions is equal to the rate of reduction of ferric ions. This reaction rate is equivalent to the exchange current.

Thus:

$$\overleftarrow{i}_{Fe^{++}} = \overrightarrow{i}_{Fe^{+++}} = i_o \qquad (I)$$

where $\overleftarrow{i}_{Fe^{++}}$ = current density equivalent to the rate of oxidation of ferrous ions; $\overrightarrow{i}_{Fe^{+++}}$ = current density equivalent to the rate of reduction of ferric ions; and i_o = exchange current density.

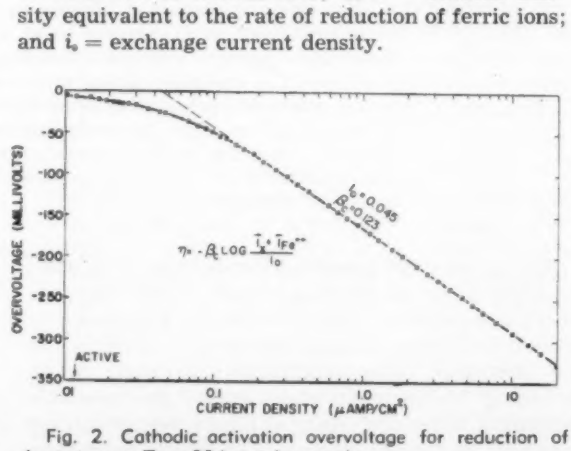

Fig. 2. Cathodic activation overvoltage for reduction of ferric ions on Type 304 stainless steel

The rate of oxidation or reduction as a function of potential is described by Eqs. (II) and (III).

$$\eta = \beta_A \log \overleftarrow{i}_{Fe^{++}}/i_o \qquad \text{(II)}$$

$$\eta = -\beta_C \log \overrightarrow{i}_{Fe^{+++}}/i_o \qquad \text{(III)}$$

where β_A is the Tafel slope for the oxidation reaction and β_C is the Tafel slope for the reduction reaction. Neither of these relations is observed experimentally at potentials close to the equilibrium potential because the reverse reaction is significant. That is, during low current cathodic polarization, the rate of oxidation of ferrous ions is of the same order of magnitude as the rate of reduction of ferric ions. The equations that describe experimental observations for anodic and cathodic polarization are

$$\eta = \beta_A \log \frac{\overleftarrow{i}_z + \overrightarrow{i}_{Fe^{+++}}}{i_o} \qquad \text{(IV)}$$

$$\eta = -\beta_C \log \frac{\overrightarrow{i}_z + \overleftarrow{i}_{Fe^{++}}}{i_o} \qquad \text{(V)}$$

where $\overleftarrow{i}_z$ and $\overrightarrow{i}_z$ are the applied anodic and cathodic current densities, respectively.

Cathodic polarization.—Fig. 2 is a plot of overvoltage as a function of applied cathodic current density. Deviation from Tafel behavior occurs at low values of applied current as expected from Eq. (V). At current densities greater than 20 μa/cm^2, an *IR* drop error was introduced. These data are not included. It is important to note the similarity between the shape of this experimental curve and shape derived from theory (3). The experimental values for β_C and i_o are 0.123 v and 0.045 μa/cm^2.

Anodic polarization.—Anodic polarization for the same system is shown in Fig. 3. In this case, deviation from Tafel behavior occurs both at low currents and at high currents. The experimental data up to 3 μa/cm^2 follow the relation described by Eq. (IV). The values of β_A and i_o are 0.102 v and 0.045 μa/cm^2. The deviation from Tafel behavior at currents greater than 3 μa/cm^2 is due to the fact that a potential region is reached where an additional oxidation reaction occurs at a rate of the same order of magnitude as the rate of oxidation of ferrous ions.[2] For the system described here, the most logical choice of this additional oxidation reaction is oxidation of water to produce oxygen, since deviation occurs in the potential range more noble than the estimated reversible potential for the reaction $2H_2O = O_2 + 4H^+ + 4e$ in the experimental environment. As illustrated previously (3), if two activation controlled reactions occur at comparable rates, the polarization curve obtained is the sum of the individual Tafel slopes. In this region, the rate of oxidation of ferrous ions plus the rate of oxidation of water are equivalent to the total applied anodic current at any given overvoltage value.

$$\overleftarrow{i}_z - \overleftarrow{i}_{Fe^{++}} = \overleftarrow{i}_w \qquad \text{(VI)}$$

where $\overleftarrow{i}_w$ is the current density equivalent to the rate of oxidation of water. Thus $\overleftarrow{i}_w$ may be calculated as a function of η. These data are shown in Fig. 3. Since the reversible potential for this reaction is unknown, a value for the exchange current cannot be calculated. β_w is 0.042 v.

[2] This same behavior was observed on a variety of passive surfaces and will be illustrated later.

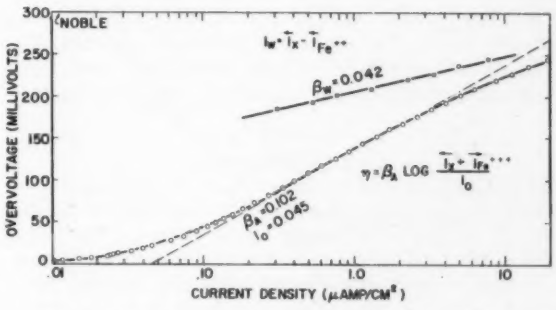

Fig. 3. Anodic activation overvoltage for oxidation of ferrous ions and water on Type 304 stainless steel.

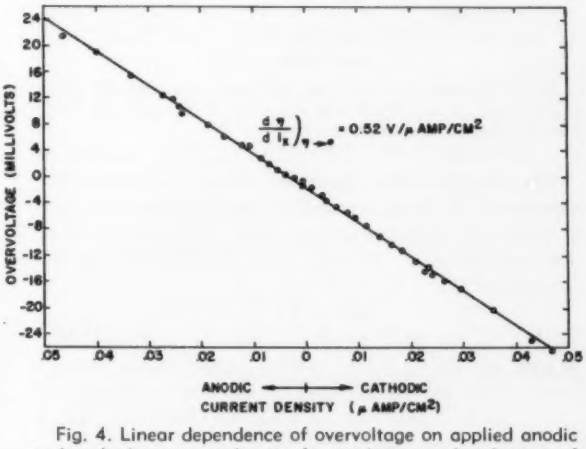

Fig. 4. Linear dependence of overvoltage on applied anodic and cathodic current density for oxidation and reduction of ferrous and ferric ions on Type 304 stainless steel.

Analysis of Low Current Data

Linear relation between overvoltage and applied current.—For overvoltage values close to the reversible potential, it can be shown[3] that

$$\frac{d\eta}{d\overleftarrow{i}_z}\Big)_{\eta\to 0} = -\frac{d\eta}{d\overrightarrow{i}_z}\Big)_{\eta\to 0} = \frac{\beta_A \beta_C}{(2.3)(i_o)(\beta_A+\beta_C)} \qquad \text{(VII)}$$

A linear plot of low current anodic and cathodic data is shown in Fig. 4. The experimental value of $\frac{d\eta}{d i_z}\Big)_{\eta\to 0}$ is 0.52 v/μa/cm^2. The value calculated from Eq. (VII) is 0.54 v/μa/cm^2. This agreement and the discussion which follows on stoichiometric number establish the validity of Eq. (VII).

Eq. (VII) proves quite valuable because it can be used to calculate one of the β values if concentration polarization, or an interfering reaction limits an experimental determination at high currents. Thus, a cathodic polarization measurement, which yields $\frac{d\eta}{d\overleftarrow{i}_z}\Big)_{\eta\to 0}$, i_o, and β_C, may be used to calculate the slope of the anodic curve.

[3] See Appendix.

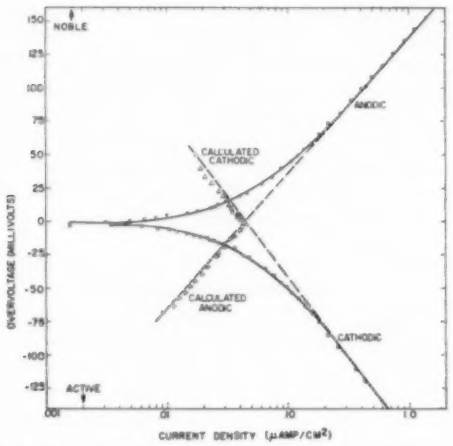

Fig. 5. Comparison of calculated and measured activation overvoltage for oxidation and reduction of ferrous and ferric ions on Type 304 stainless steel.

The stoichiometric number.—The stoichiometric number, ν, is equal to the number of times the rate-determining reaction occurs when the over-all reaction occurs once. It may be calculated from the equation (2):

$$\nu = \frac{nF\, i_o}{RT}\left(\frac{d\,\eta}{d\,i_x}\right)_{\eta\to 0} \qquad \text{(VIII)}$$

Combining this with Eq. (VII) yields

$$\nu = \frac{nF\,\beta_A\,\beta_C}{2.3\,RT(\beta_A+\beta_C)} \qquad \text{(IX)}$$

Thus, ν may be determined exclusively from high current polarization measurements or from a knowledge of i_o and low current data. The stoichiometric number calculated from Eq. (VIII) is 0.92. Eq. (IX) yields a value of 0.95. The equations thus yield consistent results.

Direct calculation of reverse reaction rates.—In addition to using Eq. (VII) to calculate the β value of the reverse reaction, Eqs. (IV) and (V) permit the direct calculation of the reverse reaction current as a function of potential. Thus, one may calculate the rate of reduction of ferric ions, $\vec{i}_{Fe^{+++}}$, as a function of η during anodic polarization or the rate of oxidation of ferrous ions, $\overleftarrow{i}_{Fe^{++}}$, during cathodic polarization. This yields the extrapolation of the cathodic activation polarization curve on the noble side of the equilibrium potential and the extrapolation of the anodic activation polarization curve on the active side of the equilibrium potential.

Fig. 5 shows an expanded view close to the reversible potential of the experimental curves presented in Fig. 2 and 3. The calculated values of $\overleftarrow{i}_{Fe^{++}}$ and $\vec{i}_{Fe^{+++}}$ fall very close to the extrapolation of the high current activation polarization curves. Thus, for any electrode whose potential is determined by the intersection of two activation polarization curves, the local anodic polarization curve can be calculated from precise measurements of cathodic polarization. The converse is also true.

If three electrode reactions are occurring at comparable rates, the Tafel constants of two of the reactions must be known in order to calculate the third. An example of this situation will be illustrated in a future discussion.

Effect of Nitrate Additions

Measurements of the type illustrated here for Type 304 stainless steel in ferric and ferrous sulfate solutions have been conducted on a variety of passive surfaces in ferric chloride in connection with studies of the pitting mechanism. Sodium nitrate was added to several of the systems studied to inhibit the pitting process and allow an evaluation of the effect of alloy type on ferric ion reduction kinetics. In order to determine whether nitrate affects the reduction kinetics of ferric ions as well as the oxidation (pitting) of the metal, nitrate was added to the ferric-ferrous sulfate solution, where pitting does not occur, and the overvoltage behavior of Type 304 stainless steel measured. The experiment is a duplicate of that described above with the exception that the solution also contained 0.4*N* $NaNO_3$. It was found that nitrate additions to solutions of ferric-ferrous sulfate or chloride do not affect the equilibrium potential as measured with a platinized Pt electrode. The data obtained were similar to those illustrated in Fig. 1-5 and are presented in tabular form for conservation of space.

Table I compares the various electrochemical constants obtained with and without nitrate. The data show that nitrate ions do not affect the activation overvoltage values to any great extent. The exchange current and β_A are decreased while β_C is unaffected. Part of the decrease in i_o may be attributed to the fact that the reversible ferric-ferrous potential for the two experiments differs by about 10 mv. It will be shown later that the exchange current decreases with a shift in the equilibrium potential in the noble direction caused by a decrease in ferrous ion concentration.

Discussion

The agreement between experimental observations and theoretical equations has been amply demonstrated. Application of the equations to a limited

Table I. Electrochemical constants for activation overvoltage of ferric and ferrous ions in sulfate solutions on Type 304 stainless steel

Nitrate content	$Fe^{+++}-Fe^{++}$ potential (I) (v)	η corr. (II) (v)	β_C (v)	β_A (v)	β_{av} (v)	i_o (μa/cm²)	$\left(\frac{d\,\eta}{d\,i_x}\right)_{\eta\to 0}$ (III)	p (IV)	p (V)
None	0.7695	0.001	0.123	0.102	0.042	0.045	0.52	0.92	0.95
0.4*N*	0.7805	0.001	0.123	0.089	0.045	0.026	0.84	0.86	0.87

(I) Standard H_2 scale; (II) Potential 304 vs. Pt in same solution; (III) V/μa/cm²; (IV) Calculated from Eq. (VIII); (V) Calculated from Eq. (IX).

amount of experimental work provides a means for calculating many of the electrochemical constants. Thus, the amount of experimental work required for a complete analysis is greatly simplified. The equations also supply a method for the determination of electrochemical constants when experimental difficulties such as concentration polarization are encountered.

More important from a practical viewpoint is the fact that the analysis also applies to a corroding electrode whose potential is determined by two intersecting activation overvoltage functions. The low current analysis should be particularly helpful here because measurements are conducted with currents of the same magnitude as the corrosion current. This minimizes the possibility of surface changes caused by high values of applied currents.

Another of the more interesting aspects of this analysis from the corrosion standpoint arises from consideration of area effects. Current density data presented above were calculated on the basis of the measured geometric area. The same exchange current density was found for anodic and cathodic polarization. This is best explained by considering the surface sites for oxidation of ferrous ions as equivalent to the sites for reduction of ferric ions. Thus, at any one instant, half of the available sites function as anode while the other half serve as cathode. This concept is supported by observation that low current measurements, where area changes should be minimized, conform with high current measurements when the data are used in equations such as (VII), (VIII), and (IX).

This situation need not apply for corroding systems where different ratios of anode-to-cathode area may be encountered. When the analysis considered here for a reversible electrode is applied to a corroding system, the exchange current in the equations becomes the corrosion current. Thus, it may be possible to calculate area ratios by comparing corrosion currents determined both from anodic and cathodic high current measurements. Also, comparison of low current data with high current data may indicate area changes during polarization. Such a treatment, if proved experimentally, may provide the first useful device for determining anode-cathode area ratios so important in corrosion studies.

APPENDIX

Derivation of Eq. (VII)

Consider an electrochemical system the potential of which is determined by two intersecting activation polarization curves whose slopes are β_A and β_C. If current from an external source is applied to such a system, then the following well-known relation applies.

$$\vec{i}_z = i_0 \left[10^{-\frac{\eta}{\beta_C}} - 10^{+\frac{\eta}{\beta_A}} \right] \qquad (X)$$

For small values of overvoltage, where $10^{-\frac{\eta}{\beta_C}}$ may be approximated by $1 - \frac{\eta}{\beta_C}$ (2.3) and $10^{+\frac{\eta}{\beta_C}}$ may be approximated by $1 + \frac{\eta}{\beta_A}$ (2.3), Eq. (X) reduces to

$$\vec{i}_z = i_0 \left(1 - 2.3 \frac{\eta}{\beta_C} - 1 - 2.3 \frac{\eta}{\beta_A} \right) \qquad (XI)$$

Rearranging produces

$$i_z = 2.3\, i_0\, \eta \left(\frac{\beta_C + \beta_A}{\beta_C\, \beta_A} \right) \qquad (XII)$$

Differentiation of overvoltage in respect to applied current results in Eq. (VII). For a corroding system, the exchange current in Eq. (X) would be replaced by the corrosion current.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1958 JOURNAL.

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Mechanisms of Hydrogen Producing Reactions on Palladium

IV. Electrochemical Kinetics of the α-Palladium-Hydrogen System in Acid Solutions

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ABSTRACT

An experimental investigation of the electrochemical kinetics of the α-palladium-hydrogen system was made by means of a palladium bi-electrode. The pH effect on the anodic and cathodic polarization behavior was determined and related to bi-electrode mechanisms. Thickness of the bi-electrode had no significant effect. It was found that catalytic activity for the hydrogen-producing reactions on α-Pd was definitely less than that on β-Pd. The fraction of the total current carried by proton flow in the bi-electrode was determined.

Studies of the mechanisms of hydrogen-producing reactions on Pd reported in earlier papers from this laboratory (1-3) were all concerned with the β-palladium-hydrogen system. The present paper is concerned with the anodic and cathodic behavior of an α-Pd-H system. Let it be defined that β-Pd is the phase in which the Pd d-bands are completely filled with electrons from H atoms (H/Pd~0.6). The alpha phase is the one in which there are positive holes in the d-bands.

Upon cathodic polarization, a Pd electrode absorbs H and tends toward the β-phase. In order to maintain a reproducible α-phase electrode, it is necessary to prevent the accumulation of H in the interior of the metal. This can be readily done experimentally by means of a Pd bi-electrode. A diagrammatic sketch of the electrode arrangement for such an experiment is shown in Fig. 1. The electrolytic cell using a bi-electrode is in fact a series arrangement of two cells, for which one side of the Pd diaphragm serves as the cathode in the first cell and the other side serves as the anode in the second cell. Since by such an arrangement there is an equivalent amount of reduction reaction on the cathode side as there is oxidation reaction on the anode side of the bi-electrode, and since H under these conditions is transported rapidly through the Pd as protons (4), there will be no tendency for the H to accumulate in the interior of the Pd. Hence by such an experimental device the Pd can be maintained at the maximum α-phase H concentration (atom ratio H/Pd = 0.03) (5) and its anodic and cathodic polarization behavior can be determined readily.

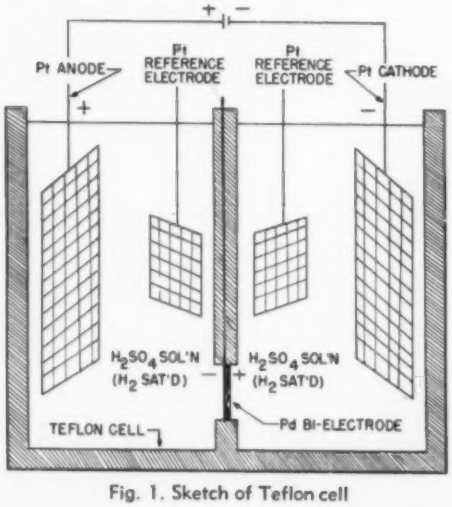

Fig. 1. Sketch of Teflon cell

An interesting aspect of the Pd bi-electrode is the fact that it is a metal membrane which is simultaneously a good electron and proton conductor. Because of this, the bi-electrode behaves as two self-depolarizing electrodes.

Experimental

The experimental technique was essentially the same as that reported in previous papers (1-3). The electrolytic cell was the same as that used in references (2, 3) except that the electrical connections were those shown in Fig. 1. The same solution was added to both compartments and the solution in both sides was stirred with H. Measurements were made with $2N$ H_2SO_4 (pH = 0); $0.3N$ H_2SO_4 + $0.7N$ Na_2SO_4 (pH = 0.9); $0.1N$ H_2SO_4 + $1N$ Na_2SO_4 (pH = 1.7). The pH values were determined at the conclusion of a run. Thicknesses of the Pd foil used as bi-electrodes were 0.001, 0.002, 0.003, and 0.004 in.

The solution resistance between the reference electrodes in both compartments and each side of the Pd bi-electrode was determined by interrupter measurements before each run.

The temperature was maintained at 31° ± 2°C. The exposed area of the Pd was 0.14 cm^2. All of the bi-electrode foils were made of annealed, hole-free metals.

All electrode potential measurements were made with respect to a Pt/H_2 electrode in the same solution. These potentials are termed overvoltages, η. This definition of overvoltage resulted in an open-circuit, steady-state, reversible potential of the α-Pd-H electrode of 0.0495 ± 0.0005 v.[1] The fact

[1] An explanation of the thermodynamics of this electrode system is presented in a paper entitled "Electrochemical behavior of the palladium-hydrogen system. I. Potential-determining mechanisms" by S. Schuldiner, G. W. Castellan, and J. P. Hoare, submitted to the "Journal of Chemical Physics."

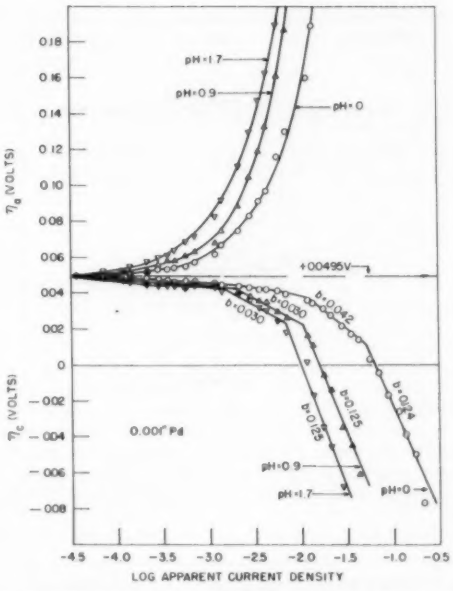

Fig. 2. Effect of pH on the hydrogen overvoltage of a Pd bi-electrode.

that this Pd had the maximum α-phase H concentration was confirmed by resistance and coulometric measurements and also by analytically determining the H content of the Pd (5).

Before the beginning of a run it was necessary to anodize (10 ma for about 45 min) both sides of the bi-electrode and then after opening the circuit to let each side of the bi-electrode reach its reversible potential (0.0495 v) in the H-saturated solution. This may require 2-3 hr. It was observed that initially the successive applications of current cause significant changes in the true area of the Pd-electrode surfaces. With repeated application of current in both an increasing and a decreasing stepwise

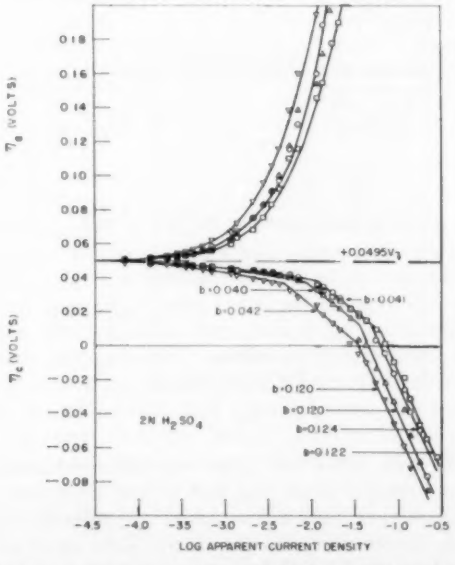

Fig. 3. Hydrogen overvoltages of Pb bi-electrodes of different thicknesses. Open circle, 0.001 in.; open triangle, 0.002 in.; inverted triangle, 0.003 in.; open square, 0.004 in.

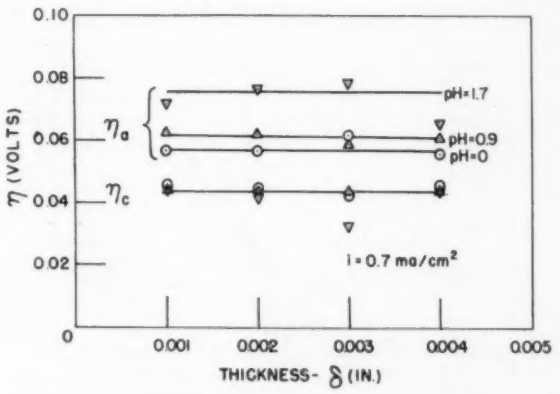

Fig. 4. Plot showing lack of thickness effect on η of Pd bi-electrodes.

fashion the area became effectively constant and reproducible time-independent measurements were possible (±2 mv). Steady-state potentials were reached within seconds after the current density was changed. The experimental results for the cathodic measurements given in this paper are the average values for each point of three separate runs in which the current was increased and decreased three times over the entire current range for each run. Those for the anodic polarization represent only the values for increasing current, because of the extremely long time required for the anodic potentials to come to steady state for decreasing currents. During a run it must be noted that coming down the current scale to open circuit conditions it was necessary that the reversible potentials on both sides of the bi-electrode be reached before obtaining measurements again at increasing currents.

Results

The overvoltage vs. log current density relationships for both the anodic polarization (η_a) and the cathodic polarization (η_c) on the Pd bi-electrode are shown in Fig. 2 and 3. Fig. 2 shows the *p*H effect and Fig. 3 shows the effects of bi-electrode thickness. Actually the thickness effect can be considered as negligible. This is shown in Fig. 4 where a low current density comparison is made. It is believed that the separation of the curves at higher current densities as shown in Fig. 3 is due to the differences in true areas of the electrodes. This area effect of the electrodes would be most apparent in the η vs. log i regions of higher slope.

Fig. 5 shows the effect of *p*H on the linear portion of η_a and η_c vs. current density curves. The fact that these curves are straight lines all passing through the 0.0495 voltage axis at zero current shows that the α-Pd-hydrogen electrode is a reversible electrode with a value of 0.0495 ± 0.0005 v vs. Pt/H_2 in the same solution.

The reciprocals of the slopes of the η vs. i curves in Fig. 5 are numerically equal to the rate constants for the over-all hydrogen producing reactions at low current densities (1, 6). A plot of these rate constants against *p*H yields the equation given below for α-Pd. A comparison of the rate constants ($di/d\eta$) in acid solutions (pH = 0 to ~ 3) for β-Pd, Pt, and

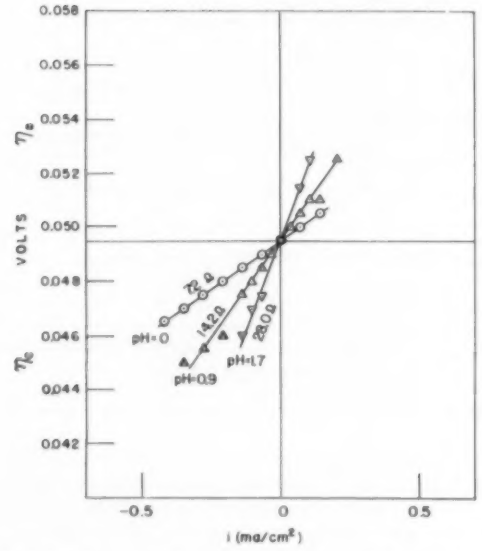

Fig. 5. The pH effect on the linear portion of η vs. i curves.

α-Pd, where in all cases the apparent current density was used in the calculation, is:

$$\beta\text{-Pd:} \quad -(di/d\eta) = 4.07 - 1.96 \ \text{pH}$$
$$\text{Pt:} \quad -(di/d\eta) = 0.356 - 0.104 \ \text{pH}$$
$$\alpha\text{-Pd:} \quad -(di/d\eta) = 0.134 - 0.061 \ \text{pH}$$

These results show that the catalytic activity of α-Pd is definitely lower than the catalytic activity for the hydrogen producing reactions of β-Pd. Since the roughness factor of Pd compared to Pt is significantly greater, a comparison of rate constants of these electrode systems using the apparent current density in the calculation is only qualitative.

Results similar to Fig. 2, 3, and 5 were obtained for all four thicknesses of bi-electrodes in the three solutions of different pH.

Discussion

Fig. 2 and 3 show three distinct η_c vs. log i regions. The first is a non-Tafel region; the second region shows a Tafel slope of either 0.03 or 0.04 depending on the pH of the solution; and the third region shows a Tafel slope of 0.12. From an analysis of the kinetics of electrode processes (1, 7) the 0.03 slope represents an atomic combination controlled mechanism, whereas 0.04 represents a mechanism which is controlled by the electrochemical desorption step.

The first of three diagrams, Fig. 6a, represents the postulated primary mechanisms for the first region (non-Tafel). On the cathode side, the reduction is hydronium ions to hydrogen atoms at the electrode surface. The hydrogen atoms move to the interior where they lose their electrons to the d-bands of palladium atoms. The protons migrate to the anode side where they regain their electrons and move to the anode surface as hydrogen atoms. At the anode surface the atoms lose their electrons and are removed from the surface as hydronium ions. The major over-all reaction in this region is the transfer of hydrogen ions from one cell to the other.

Fig. 6b indicates the principal electrode mechanisms postulated for the Tafel region for b slopes of

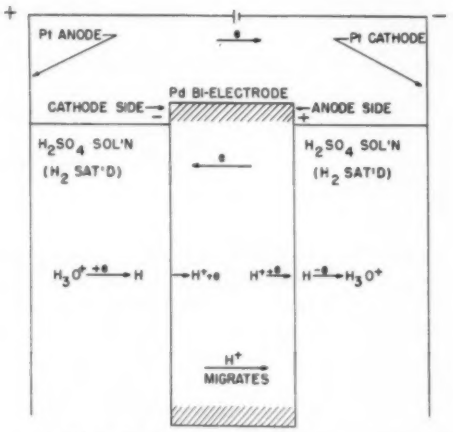

Fig. 6a. Principle electrode mechanisms of the Pb bi-electrode: a, in non-Tafel region; b, in region where Tafel slope is either 0.03 or 0.04; c, in region where Tafel slope is 0.12.

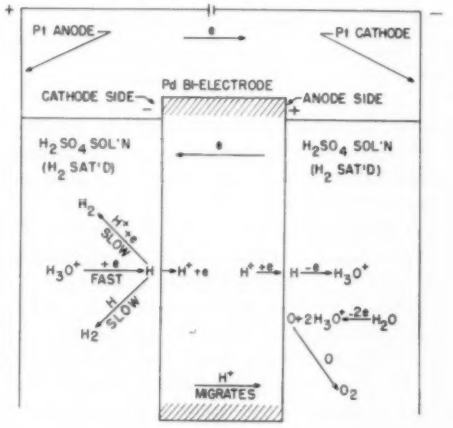

Fig. 6b

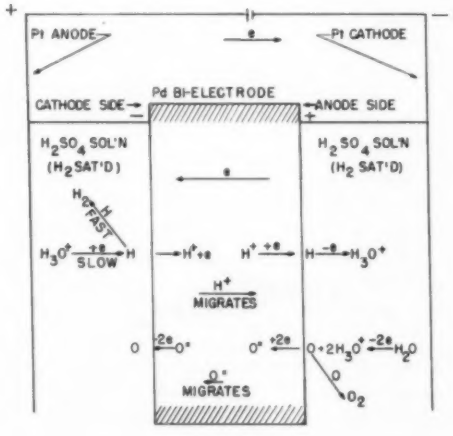

Fig. 6c

0.03 or 0.04. Here the same over-all mechanism of proton transfer from one cell to the other still occurs; however, only a fraction of the current is used in this mechanism. On the anode side, most of the oxidizing current goes into the production of oxygen and an equal portion of the reducing current on the cathode side goes into a molecular hydrogen-produc-

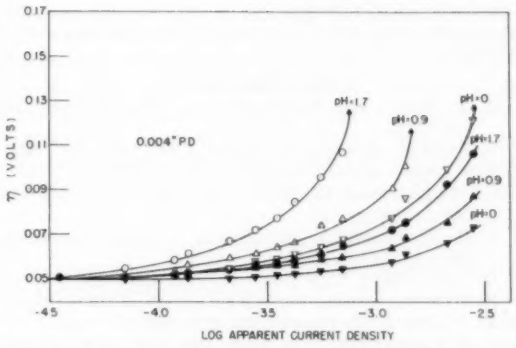

Fig. 7. Comparison of the anodic polarization of the anodic side of a Pd bi-electrode and of a simple Pd anode in solutions of various pH values. Open symbols refer to the simple anode and filled-in symbols refer to the bi-electrode.

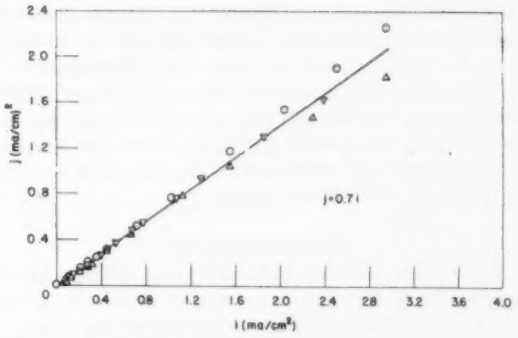

Fig. 8. Proton flow through Pd bi-electrode as a function of current density. Open circle, pH = 1.7; open triangle, pH = 0.9; inverted triangle, pH = 0.

ing reaction controlled either by the slow atomic combination step ($b = 0.03$) or by the slow electrochemical desorption step ($b = 0.04$), depending on pH.

Fig. 6c shows the postulated mechanisms for the Tafel range with a b slope of 0.12. Under these current conditions only a small portion of the current is used in transferring protons across the bi-electrode. Most of the current goes into the production of oxygen on the anode side and the production of hydrogen on the cathode side. Because of the rapid formation of oxygen on the anode side, the concentration of atomic oxygen is high enough so that a significant amount of oxygen could be dissolved in the Pd in the ionic form (8,9). The oxygen ions migrate to the cathode side, where they form atomic oxygen and subsequently exist as an oxygen or oxide particle on the surface. This oxygen can be removed by reaction with hydrogen on the surface, but Ubbelhode and Egerton (10) have shown that the removal of oxygen from the surface of Pd is a slow process. The oxygen on the surface effectively poisons the catalytic activity of the surface for the hydrogen-producing reaction. The experimental data in Fig. 2 and 3 indicate that at high current densities the poisoning of the surface with oxygen slows the hydronium discharge step more than the hydrogen combination step. This results in a change to a Tafel slope of 0.12.

Fig. 7 compares the anodic polarization on a Pd bi-electrode in various pH solutions with the anodic polarization of a simple Pd anode with the same surface. The curves for the bi-electrodes were determined in the manner described in the experimental section of this paper. The curves for the simple anodes were determined by covering the cathode sides of the same bi-electrodes with polyethylene and thus isolating that side of the electrode from the solution in that compartment. The Pd was then connected to the current source as an anode and its overvoltage, η, was determined. By comparing the two sets of curves for a given pH (simple anode vs. anode side of bi-electrode) at a definite value of η, the difference in the two current values obtained is defined as j. This j represents the amount of proton current density which is necessary to reduce the overvoltage of a simple anode to the same value as that found on the anodic side of the bi-electrode. This assumes that the same relationship between η and i exists for both electrode systems. This assumption is probably not quite correct; however, since the rate of change of overvoltage with current is small for the major portion of the current density range given in Fig. 7, any discrepancies due to variation in the η vs. log i relationship would be negligible. A plot of the relationship between j and i is given in Fig. 8. This represents the proton flow through the Pd bi-electrode as a function of current density, i. As can be seen, there is a linear relationship between j and i which is independent of pH and, as shown by Fig. 4, of thickness. The equation for this relationship is:

$$j = 0.7\, i$$

The constant 0.7 is independent of solution pH and current density as is shown in Fig. 8. It is interesting to note that, of the current carried by the Pd metal conductor between the cathode and the anode surfaces of the bi-electrode, 70% is proton current and 30% is electron current. In terms of the Pd bi-electrode as shown in Fig. 6, this means that at the low current density range 70% of the applied current goes into the transfer of hydrogen ions from the first cell to the second and 30% goes into the production of the products of the reduction reaction on the cathode side and the oxidation reaction on the anode side. The reason could be that on the cathode side of the bi-electrode the transfer of adsorbed hydrogen atoms on the Pd surface through the skin of the metal to protons in the interior of the metal is slow enough so that some surface desorption of atomic hydrogen takes place. Similar conditions exist on the anodic side of the bi-electrode. This postulate is supported by the absence of a thickness effect of the bi-electrode.

In another series of experiments, one side of the Pd membrane was made an anode without blocking off the other side with polyethylene so that this side of the metal was in contact with a hydrogen-stirred H_2SO_4 solution. In these experiments the Pd was a simple anode as in the experiment above, with the exception that in this case the back side of the Pd anode was in contact with the hydrogen-saturated solution. The anodic overvoltage curves obtained for this system at low current densities were in all

cases not significantly different from the overvoltage curves obtained for the anodic side of the bi-electrode for solutions of the same pH. Deviations occurred at the higher current densities. These results indicate that at low current densities hydrogen ion transfer took place with equal ease from the first cell to the second cell whether the Pd was used as a bi-electrode or as a simple anode.

Acknowledgments

The authors are indebted to Dr. J. C. White for his suggestion of a study of the Pd bi-electrode system and for his advice during the course of the work.

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Any discussion of this paper will appear in a Discussion Section to be published in the June 1958 JOURNAL.

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Kinetics of Metal Deposition

Significance of Experimental Data and Some Results Using Voltammetry at Constant Current

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ABSTRACT

The discharge characteristics of the deposition of lead, thallium, silver, bismuth, copper, tin, and antimony ions onto the solid metals, using constant current voltammetry, are reported and discussed.

At least two parameters are needed to describe deposition onto solid surfaces that are not required when working with mercury electrodes. These are (*a*) a roughening factor, *f*, which may be defined as the ratio to the geometrical area of the surface area effective for the transport of discharging molecules, and (*b*) a reactivity factor, β, which is the ratio to the geometrical area of the area reactive to the discharge process.

A direct comparison of kinetic data for solid metal deposition obtained by different methods is not valid unless these measurements are made while the metals are being continuously deposited at comparable current densities and from identical solutions.

In the past decade, new methods for studying electrode kinetics, in particular the use of superimposed alternating voltage and electrolysis at constant current, have been used with a mercury electrode. However, with a few exceptions, these new techniques for kinetic study have not been employed with electrodeposits of solid metals, workers having naturally preferred to use a mercury surface where the geometrical surface area of the metal can be assumed to be identical with the area governing the transport of molecules and their subsequent discharge. With any attempt to study the discharge at a solid metal surface formidable experimental difficulties arise. A discussion of the significance of experimental data in this field and a summary of the parameters that can be obtained by modern methods are given here since most of the published formulas relate either to oxidation-reduction processes, in which both species are in solution, or to the depositions of metals into mercury to form amalgams.

General Kinetic Equations

It is common practice to write the equations for the rate of deposition processes in terms of an exchange current and Tafel slope although, as electrode kinetics are a particular case of heterogeneous chemical processes, assisted, or otherwise, by an applied potential, it would appear more logical to express reactions in terms of a heterogeneous kinetic constant of dimensions LT^{-1} and a parameter α, the transfer coefficient, showing what fraction of the applied potential assists the discharge process. It is general to write a basic equation in the form:

$$i = i_f - i_b = nFA_r \left[k_f C_r e^{\frac{\alpha nF}{RT}E} - k_b e^{-(1-\alpha)\frac{nF}{RT}E} \right] \quad (I)$$

In this equation, i is the cathodic current in amperes and C_r is the concentration of the discharging species at the electrode surface at an applied potential of E, which is here taken as the electrode potential on the hydrogen scale using the Lewis-Randall sign convention. Alpha is the fraction of the potential drop at the electrode surface, assumed to vary linearly with distance over the metal-solution interface, which assists the discharging species to surmount any energy barrier between its initial and discharged

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states. A_r is the area of electrodes which is reactive to the discharge process, F is the Faraday, and n the number of electrons involved in the rate-determining step. This step is not necessarily the same as the complete discharge reaction when multivalent changes take place but will probably be so for the more simple ionic discharge reactions. This type of discharge kinetics gives rise to what Vetter (1) describes as a "penetration" overvoltage and is the only kinetic step considered in this discussion.

The constant k_f in Eq. (I) has the dimensions LT^{-1} of a first order heterogeneous reaction constant, but k_b, unlike the back-reaction constant for a redox reaction, has the dimensions $L^{-3}T^{-1}$. Both constants contain a voltage term, as E in Eq. (I) is measured from an arbitrary potential level. It may be argued that a reaction constant, k°_f, should really be used, this constant applying when the potential between the metal surface and discharging species, centered some few Angstrom units from the metal-solution interface, is truly zero. Approximations to this potential could be used, such as the electrocapillary zero or the potential at which the χ potential is zero (2) or, following Mattsson (3), a potential where the difference between the galvani potential and a potential taken from infinity in the solution phase to the outside of the Helmholtz layer is zero. However, the value of such a potential is unknown, and probably unknowable, and the constants k_f and k_b, as defined by Eq. (I), are at present the only practicable parameters.

Values of k_f for discharge of a metal ion into an alloy (the most common instance is in forming an amalgam) cannot be compared directly with the k_f values found when the same ion discharges into the lattice of a pure metal, as the zero interface potential will probably be markedly different in the two cases. It is unlikely, however, that differences in k_f of much more than about one or two orders of magnitude result from this cause.

On defining a fraction:

$$\beta = A_r/A$$

where A is the geometrical area of the electrode, Eq. (I) becomes

$$I = I_f - I_b = nF\beta\left[k_f\, C_r\, e^{\frac{\alpha nF}{RT}E} - k_b e^{-(1-\alpha)\frac{nF}{RT}E}\right] \quad \text{(II)}$$

where I is the apparent current density on the solid metal, which can be directly measured, and concentrations are expressed as moles/cc.

If E_r is the reversible (zero current) potential of the electrode in a solution containing a bulk and surface concentration of C moles/cc; as $I_f = I_b$ when E equals E_r:

$$E_r = \frac{RT}{nF}\ln\frac{k_b}{k_f} - \frac{RT}{nF}\ln C$$

Comparing this with the Nernst equation:

$$E_r = E^\circ - \frac{RT}{nF}\ln \text{ (activity of discharging species)}$$

shows that the standard potential E° is given by:

$$E^\circ = \frac{RT}{nF}\ln\frac{k_b}{k_f}y$$

where y is a factor, related to the mean activity coefficient of the discharging species, which has the dimensions L^3.
Hence:

$$k_b = \frac{k_f}{y}e^{\frac{nF}{RT}E^\circ}$$

and Eq. (II) can be written:

$$I = nF\beta\, k^\circ\left[C_r\, e^{\frac{\alpha nF}{RT}(E-E^\circ)} - \frac{1}{y}e^{-(1-\alpha)\frac{nF}{RT}(E-E^\circ)}\right] \quad \text{(III)}$$

where:

$$k^\circ = k_f\, e^{\frac{\alpha nF}{RT}E^\circ} = k_b y\, e^{-(1-\alpha)\frac{nF}{RT}E^\circ} \quad \text{(IV)}$$

The constant k° is related to the constant k_{sh} used by Delahay (4). The use of such a constant has the advantage that it is more characteristic of a reaction than is k_f or k_b because it no longer depends in magnitude on the value of E which is measured on an arbitrary potential scale. However, E° is not known for many metal depositions reactions, unlike the corresponding value for a redox reaction which is comparatively easy to evaluate.

The apparent exchange current density, $I_{o(s)}$, is equal to $I_{f(s)}$ or $I_{b(s)}$ at the reversible potential $E_{r(s)}$, hence from Eq. (II):

$$I_{o(s)} = nF\beta\, k_f\, C\, e^{\frac{\alpha nF}{RT}E_{r(s)}} \quad \text{(V)}$$

From Eqs. (IV) and (V) and the Nernst equation, it follows that one can also write:

$$I_{o(s)} = nF\beta\, k^\circ\, y^{-a}\, C^{1-a} \quad \text{(VI)}$$

With a redox system, or where a metal is deposited into mercury, provided that the activities of oxidized and reduced forms are about equal, the equivalent equations to (V) and (VI) are:

$$I_{o(l)} = nF\, k_f\, C\, e^{\frac{\alpha nF}{RT}E_{r(l)}} \quad \text{(Va)}$$

and:

$$I_{o(l)} = nF\, k_{sh}\, C \quad \text{(VIa)}$$

The parentheses (s) and (l) in the above equations are used to denote a reaction taking place at a solid metal surface or at a mercury or amalgam surface. Eq. (II) is often written in terms of $I_{o(s)}$ and the overvoltage $\eta = (E_r - E)$ as:

$$I_{(s)} = I_{o(s)}\, e^{\frac{-\alpha nF}{RT}\eta}\left[1 - e^{\frac{nF}{RT}\eta}\right] \quad \text{(VII)}$$

or as:

$$I_{(s)} = I_{o(s)}\left[\frac{C_r}{C}e^{\frac{-\alpha nF}{RT}\eta} - e^{\frac{(1-\alpha)nF}{RT}\eta}\right] \quad \text{(VIII)}$$

where C is the bulk concentration of the discharge species. These equations can be used to determine I_o and α from experimental data by taking the extreme cases where either y is so small that an expansion of the exponentials, ignoring higher terms, is valid or y is sufficiently large for the back reaction to be negligible. In all cases, however, a determination of the $I_{o(s)}$ value for a deposition reaction onto a solid metal [Eqs. (V) and (VI)] does not

enable a velocity constant to be obtained as is the case with Eqs. (Va) and (VIa). The term ($\beta k^\circ y^{-\alpha}$) is determined. $y^{-\alpha}$ can be eliminated if E_r and E° are known or (βk_f) found from Eq. (V) if E_r alone is known.

The constants β and k° or k_f cannot be determined separately by any known method and the best approximation at present is to assume that the constants k° or k_f for a given discharge reaction are the same when the metal is deposited into mercury as when it is deposited out on a solid metal surface. This assumption may, as mentioned earlier, be subject to error and the only obvious alternative is to work with single crystal faces in highly purified solutions and assume that β is near to unity.

If the rate constants and α values for liquid and solid surfaces are assumed to be approximately equal, β can be evaluated by taking the ratio of the apparent exchange current densities $I_{o(l)}$ and $I_{o(s)}$ at the same C values. From Eqs. (V) and (Va):

$$\frac{I_{o(s)}}{I_{o(l)}} = \beta\, e^{\frac{\alpha n F}{RT}(E_{r(s)} - E_{r(l)})} \qquad \text{(IX)}$$

or from (VI) and (VIa)

$$\frac{I_{o(s)}}{I_{o(l)}} = \beta\, C^{-\alpha} y^{-\alpha} = \beta\, e^{\frac{\alpha n F}{RT}(E_{r(s)} - E^\circ_{(l)})} \qquad \text{(X)}$$

these equations being practically equivalent, as with equal activtities of oxidized and reduced forms, $E_{r(l)} \triangleq E^\circ_{(l)}$

In all experimental techniques used at present for the determination of k_f and α values some concentration polarization is encountered and must be eliminated by a suitable mathematical treatment, generally involving a solution of Fick's equation. When working with mercury the assumption is made that surface area effective for the transport process, A_r, is identical with the geometrical area A. This may well not be the case with a solid metal and a diffusion roughness factor, f, can be defined from:

$$f = At/A$$

This factor is not the same as β or as a true surface factor measured by gas adsorption, capacity measurements, or similar techniques. The factor f depends on the relative size of surface irregularities and on the thickness of the transport layer at the surface, which may or may not follow the surface contours. f may be related to β but this is not necessarily so and no generalizations can be made.

Techniques Employed

Steady-state current-voltage measurements.—Steady-state polarization curves have been used extensively to study electrodeposition on solid electrodes, but comparatively little work has been reported where transport polarization has been completely eliminated or accurately allowed for in calculations of kinetic data (5-7). The techniques and approximations are too numerous to summarize but generally I_o and α values are reported based on the solution of equations such as (VII) or (VIII). The present authors (8) have described a polarographic technique where transport by convective diffusion is allowed for and which enables α and (βk_f) to be determined for moderately slow discharge reactions. None of these methods is satisfactory for studying really fast discharge processes.

Impedance measurements with a periodically changing potential.—Work with solid electrodes in aqueous solutions has been reported by Hillson (9) in the case of Cu. The difficulties encountered when using this method arise from the fact that the behavior is not that to be expected from a uniform reactive surface. Continuous deposition does not take place to renew the metal surface during measurements. Rather, ions are leaving and entering the metal surface in equal numbers, a process which does not insure maintenance of a continuously active surface and remove impurities from solution in the vicinity of the metal. Fixed discharge centers form which are prone to poisoning; β tends to be less than the value found by methods involving continuous plating. β is critically dependent on surface preparation and is likely to change during the course of a single experiment. Other experimental complications center round the variation of double layer capacity with frequency encountered with solid surfaces (10, 11). There is doubt whether the technique shows much promise with solid electrodes despite its importance in studying discharge processes at mercury surfaces (12-17).

Ideally the method should give values for α, f and ($\beta k^\circ y^{-\alpha}$) if the diffusion coefficient D of the discharging species is known or (βk_f) if E_r is also measured. The values for f and β will be quite different than those operative during a continuous plating process and will have little fundamental significance. If R_r and R_d are the reactive and diffusive resistance of an electrode, calculated from the complex impedance by making correction for the double layer capacity;

$$R = R_r + R_d = \frac{RT}{n^2 F^2 C A}\left[\frac{1}{k^\circ y^{-\alpha} C^{-\alpha} \beta} + \frac{1}{f(2Dw)^{1/2}}\right]$$

where $R_d = \dfrac{1}{w C_d}$, C_d being the diffusive capacity, whence $R_r = \dfrac{RT}{n F I_{o(s)} A}$ can be calculated as R and C_d are measurable quantities.

The corresponding equations for the same discharge reaction on a mercury surface, where the metal dissolves and has equal activity in both phases, are:

$$R = R_r + R_d = \frac{RT}{n^2 F^2 C A}\left[\frac{1}{k_{rh}} + \left(\frac{2}{wD}\right)^{1/2}\right]$$

whence again $R_r = \dfrac{RT}{n F I_{o(l)} A}$ and $I_{o(l)}$ can be calculated.

The factor f depends on the frequency $w/2\pi$ used and will be greater than unity, if the surface is uniformly reactive, unless the surface irregularities have a radius less than about 10^{-5} cm. The surface is probably far from uniform in activity, however, and Vetter (18) has considered the case where reactive centers are present on an uneven surface.

Studies at constant current.—The use of constant current voltammetry has been revived recently and applied to kinetic studies (19-24). For a rapid dis-

charge process the equation for a "reversible" deposition process at a solid electrode is:

$$E = E^\circ - \frac{RT}{nF} \ln\left(y \frac{C}{\tau^{1/2}}\right) - \frac{RT}{nF} \ln\left(\tau^{1/2} - t^{1/2}\right) \qquad \text{(XI)}$$

where E is the voltage at time t seconds and τ is the "transition time", the time taken from first applying a current of apparent density $I_{(a)}$ until the voltage abruptly tends to infinity. As $\tau^{1/2}$ is related to the current density, being inversely proportional, a plot of E against log $(\tau^{1/2} - t^{1/2})$ will give a separate line for each value of $I_{(a)}$, but all lines will have the ideal Nernst slope of $0.0591/n$ at 25°C.

For a slow discharge process the equation:

$$E = \frac{RT}{\alpha n F} \ln\left[\frac{I_{(a)}\,\tau^{1/2}}{nFCf\beta k_f}\right] - \frac{RT}{nF} \ln\left(\tau^{1/2} - t^{1/2}\right) \qquad \text{(XII)}$$

applies at voltages in excess of about $0.1/n$ v from the reversible potential. As $(I_{(a)}\,\tau^{1/2})$ is a constant, at least over a limited range of $I_{(a)}$ values, a plot of E against log $(\tau^{1/2} - t^{1/2})$ should give only one straight line irrespective of the value of $I_{(a)}$ and the slope will be a measure of α. f can be determined independently from the equation:

$$f = \frac{2\,I_{(a)}\,\tau^{1/2}}{\pi^{1/2} n F D^{1/2} C} \qquad \text{(XIII)}$$

if D is known. From Eqs. (XII) and (XIII) (βk_f) can be evaluated. $I_{o(a)}$ follows [Eq. (V)] if E_r is measured before applying the current. Gerischer (25) has used an extrapolation technique to give the E value at zero t from which $I_{o(a)}$ and α can be found. A different but elegant method of extracting data from measurements by this technique is described by Gierst (26).

Transition times of the order of 10-100 sec are obtained using $I_{(a)}$ values of the order of 10^{-4} amp/cm². The use of short current bursts and the oscillographic measurements of potential over short time intervals (generally very much less than τ) has been described (27-29) and ideally very large k_f values could be measured by such a method, but accurate compensation is necessary for capacitive effects at the electrode surface and this is likely to give trouble with solid electrodes.

Present Investigation

The use of continuously applied constant current (in contrast to square wave current impulses) has received little attention with electrodeposition on solid electrodes. No kinetic parameters resulted from the work of Turner and Winkler (30) or from the few experiments made by Reilley and co-workers (31) in their evaluation of the constant current technique as an analytical tool. Fianda and Nagel (23) studied the deposition of Ag and found it reversible, but a correction for roughness (24) was needed and there was sometimes evidence of the presence of a highly active surface to the initial metal until deposition of a fresh surface took place. In the present work the deposition of a large number of comparatively "uncomplexed" ions, mainly perchlorates, was studied, the factor f found and reductions classified as irreversible or reversible. In the latter case, the reactions were too rapid for kinetic analysis by constant current voltammetry at $I_{(a)}$ values around 5.10^{-4} amp/cm² (or about half an amp/ft²). Values for α and (βk_f) for Bi and Cu depositions have been determined and the results compared with results obtained by other techniques.

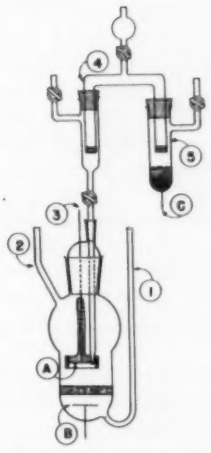

Fig. 1. Diagram of cell

Experimental Procedure

The circuit used was practically identical with that described by Delahay and Mattax (21). The cell used, however, was designed specifically for this investigation and is shown in Fig. 1. A polished Pt disk, A, acted as cathode (after plating with the metal concerned) and was fixed in a polyethylene holder and cemented into place with a mixture of Picien and paraffin wax which insulated the back of the disk and the wire lead, 3, and prevented any creep back of electrolyte. The cathode, with about ½ cm of edge shielding, was held symmetrically several cm above a Pt disk anode, B, of the same area (2.24 cm²), being separated from it by a coarse glass sinter. The cell was filled with electrolyte and deoxygenated by passing electrolytic hydrogen through tube 1 and out of tube 2 while the whole equipment was immersed in a water bath thermostatically controlled at 25° ±0.1°C. The capillary probe for measuring the working potential was less than 0.5 mm diameter at the tip and projected less than 1 mm from the back of the cathode. Although this is not perhaps the ideal arrangement (4) it seemed about the most practical and was thought to give a representative potential for the cathode surface to within 1 or 2 mv. The probe was filled with the working electrolyte and connected via a saturated ammonium nitrate salt bridge, 4, to the calomel half-cell, 5. A constant current, varying between about 0.1 and 0.4 ma in magnitude, could be passed between A and B and the potential between A and C measured against time with a L&N Speedomox recording potentiometer of about 2 seconds response time. Transition times, between about 10 and 200 sec, were recorded and the constancy of the product $(I_{(a)}\,\tau^{1/2})$ and $(I_{(a)}\,C^{-1})$ checked for a three- to fourfold variation of $I_{(a)}$ and C before voltage-time curves were taken. These products were always constant to within 1-2%. The Pt cathode was com-

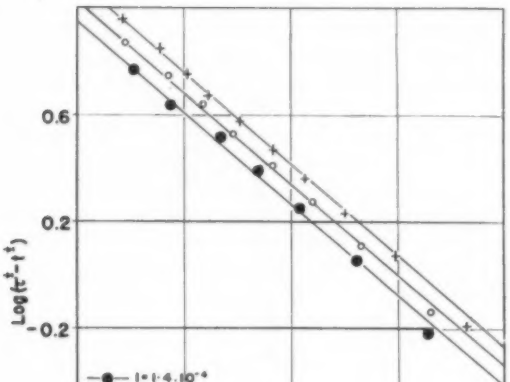

Fig. 2. Reversible reduction, 4.10^{-3}M Tl^{+} in 1M $NaClO_4$

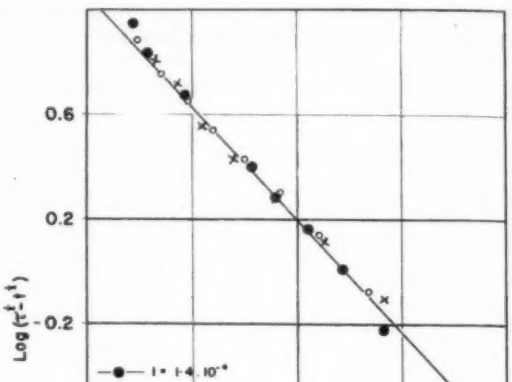

Fig. 3. Irreversible reduction, 4.10^{-3}M Cu^{2+} in 1M $NaClO_4$

pletely covered by the metal under study, after which voltage-time curves were highly reproducible from experiment to experiment.

Solutions were prepared from analytical quality reagents and the base electrolytes purified by shaking with neutral activated alumina. Diffusion coefficients and stationary electrode polarograms were determined as described previously (8). The metal salts had the same anion as the base electrolyte.

Results

The depositions studied were either reversible or markedly irreversible. An example of the former is shown in Fig. 2 for 4.10^{-3}M Tl in 1M $NaClO_4$. The slope is exactly theoretical and the separation of lines is marked even when the current density changes by only about 10%. The irreversible deposition of 4.10^{-3}M Cu in 1M $NaClO_4$ is shown in Fig. 3 where a straight line is found with potentials more cathodic than about 0.04 v. In this and other irreversible reductions all points fell on the same line, even with current density changes of 50-100%.

The quantitative results of this investigation are shown in Table I. All voltage-time curves were obtained using 4.10^{-3}M solutions in the base electrolytes shown, with apparent current densities of about $2\text{-}5.10^{-3}$ amp/cm^2, i.e., about the lowest densities used in commercial electroplating. f values were calculated from Eq. (XIII), using polarographic D values, and (βk_f) values were obtained from the plot of Eq. (XII) and thence $I_{o(a)}$ using Eq. (V). The values for (βk°) are estimates based on values for E° in Latimer (32). Data by constant current, denoted C.C., are compared with the data obtained by solid electrode polarography (8), denoted S.E.P., using the same solution for both experiments.

In addition to the experiments shown in Table I, others were made which may be reported briefly. Stannous Sn in a concentration which was undeter-

Table I. Quantitative results

Metal ion	Base electrolyte	Method	$D \times 10^5$	f	Slope	E_r	α	(βk_f)	(βk°) $\times 10^5$	$I_{o(a)} \times 10^4$ amp/cm^2
Tl	1M $NaClO_4$	C.C.	1.88	1.04	0.059	+0.47		Reversible		
		S.E.P.		1.0	0.060	+0.47		Reversible		
Ag	0.5M KNO_3	C.C.	1.50	1.06	0.058	−0.63		Reversible		
		S.E.P.		1.0	0.060	−0.63		Reversible		
Pb	1M $NaClO_4$	C.C.	0.92	1.00	0.031	+0.19		Reversible		
		S.E.P.		1.0	0.0305	+0.19		Reversible		
Bi	1M Tartaric acid	C.C.	0.41	0.98	0.0208	−0.18		Reversible		
		S.E.P.		1.0	——	−0.18		Two or more reducing species Reversible reduction for major component.		
Cu	1M $NaClO_4$	C.C.	0.68	1.00	0.092	−0.27	0.32	0.14	4.1	1.7
		S.E.P.		1.0	0.080	−0.255	0.37	0.68	5.6	4.5
Bi	1M $HClO_4$	C.C.	0.60	1.12	0.0354	−0.24	0.56	960	0.17	2.9
		S.E.P.		1.0	0.056	−0.245	0.35	10	3.25	7.4
Bi	1.0M KCl	C.C.	0.87	1.17	0.0333	−0.12	0.59	0.9	2.3	3.6
	0.1M HCl	S.E.P.		1.0	0.0345	−0.125	0.57	1.3	4.6	5.2

mined but near to 4.10^{-5}M gave reversible behavior, the slope being 0.0302 compared with the theoretical 0.0296. The plots obtained with Sb in alkali and acid were poor, indicating consecutive reductions from a solution containing more than one species of ion. This effect was least marked in acid where the mean slope was near to that expected from a reversible 3 valent reduction.

Satisfactory plots were not obtainable from data for Cd in sulfate solution or for Ni and Zn solutions in either acid or alkali. Either no transition time was obtained or it was too poorly defined to be of quantitative value.

Discussion

The constant current method, using current densities giving transition times between about 10 and 200 sec, can be used for kinetic measurements with solid electrodes, but many discharge processes of the softer metals are too rapid for measurement and are recorded as "reversible". The reversible or irreversible behavior depends on β as well as the value of k°. The discharge of Cu from perchlorate and Bi from chloride, which is reversible polarographically on Hg, presumably appears irreversible here at a solid electrode because β is much less than unity. Comparison of the $I_{s(a)}$ value obtained in this work for Cu with the $I_{s(i)}$ value calculated from the data of Randles and Sommerton (17) suggests that β is only a few per cent. A similar calculation for Bi in perchlorate gives β as nearly 100% for this softer metal, indicating that the discharge process itself is slow, as would be expected from an ion such as $(Bi\ O)^+$.

Values for f are never much greater than unity, in agreement with the microscopic appearance of the plated metals.

Data obtained by Hillson (9) on solid Cu electrodes, using the a-c bridge method, have been recalculated but show no agreement with the present work. Hillson's value for f is very small, about 2%, indicating that large areas of the electrode are inactive, and yet the apparent exchange current density is nearly one hundred times as great as found in the present work and his value for α is nearly twice as great. It appears to be of little value to compare data obtained by different methods unless the nature of these methods is such that the surface condition of the metal is reproducible and this can be ensured only by having continuous deposition of fresh metal at comparable current densities from identical solutions in both procedures. In view of this, a value of 0.43 for α and 5.10^{-4} amp/cm^2 for $I_{s(a)}$ obtained by Shreir and Smith (7) with an acid copper sulfate solution and current densities 50-100 times greater than used here, may be considered to be in general agreement. The agreement between α and k° values, obtained by constant current and by solid electrode polarography on the same solutions, is very good in the case of Cu from perchlorate and Bi from chloride. The agreement is not satisfactory with the Bi reduction from perchlorate and the reason is not at once obvious as repeat experiments by both methods gave results agreeing to within a few per cent. The polarographic result may be misleading, however, as low values for α can be obtained by this method if two or more reducible forms of the metal are present in solution. The solid electrode polarograms of Sb in tartrate, Bi in tartrate and other solutions did not give smooth curves, but what appeared to be curves arising from the reversible reduction of the metal, present in one state of combination, followed by the irreversible reduction of a minor amount of the metal combined in a less easily reducible form. Such behavior, by the nature of the method used, can give misleading information by the polarographic method, but with the constant current procedure may not give results that differ greatly from those to be expected from the predominant species alone.

The unsatisfactory behavior of Ni and Zn solutions, even in alkaline media, can be attributed to water reduction (33) and the reduction of hydrogen ions, or water, prevented repetition of the published work on cadmium sulfate. Using identical conditions to those described by Lorenz (27) it was not possible to record a transition time because of the formation of hydrogen.

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Technical Feature

Hydroelectric Power Resources of British Columbia and the Yukon

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British Columbia Electric Company, Ltd., Vancouver, British Columbia, Canada

The hydro resources of British Columbia and the Yukon are discussed. To acquire perspective at the outset, a comparison is made between these resources and the hydro resources of the other provinces of Canada. Table I, column 2, shows the present developed horsepower in Canada, with Quebec in the lead, with nearly 8 million hp, followed by Ontario, 5.3 million hp, and British Columbia in third place with 2.2 million hp. Table I, column 1, shows the undeveloped hydro potential remaining in the various provinces, again with Quebec in the lead, with some 20½ million hp, and British Columbia in second place with 11 million hp.

These figures are taken from a publication of the Department of Northern Affairs and National Resources, March 1956, and represent the best information available to the Department at the time they were compiled.

To illustrate how the picture changes as more is learned of the resources, in place of the approximately 11 million hp figure for British Columbia, use the estimate made by the Water Rights Branch of the Provincial Government in November 1955 (Table I, column 1, figure in parentheses). On the basis of the provincial figure, the undeveloped hydro potential in British Columbia is very close to that of Quebec, standing at some 23 million hp. It is not suggested that British Columbia has more undeveloped hydro potential than Quebec, since undoubtedly extension of surveys in Quebec itself will prove up still further potential.

Still dealing in general terms, something of the characteristic features of hydro power in British Columbia and how it may be developed are discussed briefly. This will serve as a background for reviewing the resources and will illustrate why there is such a wide discrepancy between the estimates of the potential power in the province as given by the Federal Department of Northern Affairs and National Resources and as given by the Provincial Government of British Columbia.

Geographically, British Columbia is a series of mountain ranges running north and south, with rather narrow valleys and little land for cultivation, arable land totalling not more than 6% of the area of the province; the two exceptions are the Peace River area, which is an extension of the northern prairies and is the site of oil and natural gas discoveries, and the Fraser River delta, which is the industrial and population center of the province. "A sea of mountains" is a phrase which has been used to describe the topography of British Columbia. Generally speaking, the moisture bearing Westerly winds sweeping in from the Pacific deposit their waters on the slopes and valleys of the mountain ranges as snow or seasonal rain; this gives rise to a great problem in utilizing the water since the rivers and streams are subject to sharp flooding in the spring and decline to comparatively meager flows in the winter months.

On large rivers in British Columbia, the ratio of high to low flows is of the order of 40 to 1 and as much as 2000 to 1 on smaller streams. By comparison, the St. Lawrence River at Lachine Rapids has a ratio of high to low water of only 2.2 to 1. Table II gives further detail on this.

In order to develop power economically in British Columbia, some artificial means is required to reduce flood flows and to increase the low winter flows. The usual means is the construction of dams to catch the spring flows and store the water until required the following winter.

The necessity for such storage obviously gives rise to rather high costs in hydro power engineering development, but as mentioned below, has directed engineering thinking along lines which will be

Table I. Available water power and developed water power in Canada at the end of 1955

	Available 24-hr power at 80% efficiency, ordinary 6 months flow hp	Installed hp
Quebec	20,445,000	7,975,657
Ontario	7,261,000	5,367,866
British Columbia	10,998,000 (22,913,000) *	2,271,460
Manitoba	5,562,000	796,900
Newfoundland	2,754,000	329,150
Alberta	1,258,000	284,010
Nova Scotia	156,000	177,018
New Brunswick	334,000	164,130
Saskatchewan	1,120,000	109,835
Yukon and N. W. T.	814,000	33,240
Prince Edward Island	3,000	1,882
Canada	50,705,000	17,511,148

Source: Dept. of Northern Affairs and National Resources, March 1956.
* Water Rights Branch, Province of British Columbia, November 1955.

Table II. Ratio of maximum to minimum flow

River	Location	Ratio max min flow
	British Columbia Rivers	
Bridge	near Bridge River	158/1
Cheakamus	Garibaldi	146/1
Lillooett	near Pemberton	141/1
Nass	Aiyansh	135/1
Kootenay	Wardner	112/1
Campbell	near Campbell River	108/1
Columbia	Revelstoke	95/1
Kootenay	Glade	42/1
Columbia	Birchbank	35/1
Fraser	Hope	33/1
Thompson	Spence's Bridge	33/1
Chilliwack	near Veddar Crossing	31/1
Fraser	Quesnel	28/1
Tahtsa	near Ootsa Lake	27/1
Ootsa	Ootsa Lake	26/1
Stuart	near Fort St. James	19/1
Nechako	near Fort Fraser	13/1
	Eastern Rivers	
St. Maurice	Bergeron's	12.2/1
Ottawa	near Temiskaming	9.3/1
Nipigon	below Vugin Falls	8.5/1
Winnipeg	above Boundary Falls	6.2/1
St. Lawrence	Lachine Rapids	2.2/1

Source: Dominion Water & Power Bureau, 1945.

highly profitable in the future in improving the hydro potential of the province.

The estimate of hydro potential so far used by the Department of Northern Affairs and National Resources is derived from studies made over a number of years, taking into account the volume of water flowing at various times in the year and assuming that hydro plants would be installed in the various river channels where conditions appear favorable. The estimates did not include the very large developments which could be realized by diversion of several rivers into entirely different watersheds.

As well as being a land of mountains, British Columbia is a land of sharp valleys gouged by the passage of glaciers in ages past. Recent techniques for water power development have centered on making use of the differing elevations of valleys on either side of a mountain range to provide head for power generation. The various combinations of storage water, free stream flow, and diversion from one watershed to another are well illustrated by Fig. 1 which is an artist's sketch of the Bridge River power plant system of the B.C. Electric Company Ltd. At the top of the diagram is shown the La Joie reservoir which impounds 570,000 acre-feet of water. The dam contains 3¾ million ft³ of material and is 282 ft high, providing head for a 30,000 hp turbine to be installed in 1957. At present a dam diverts the water released from the La Joie reservoir into a tunnel passing through Mission Mountain to fall 1100 ft to the generating station on Seton Lake; eventually a new dam will impound water to form Lake Carpenter. The present capacity of this station is 248,000 hp and is being increased to an ultimate 600,000 hp capacity. Finally, at the outlet of Seton Creek, a 58,500 hp unit uses the water a second time as it is released from the Seton Lake generating plant and is essentially a run-of-the-river type of plant.

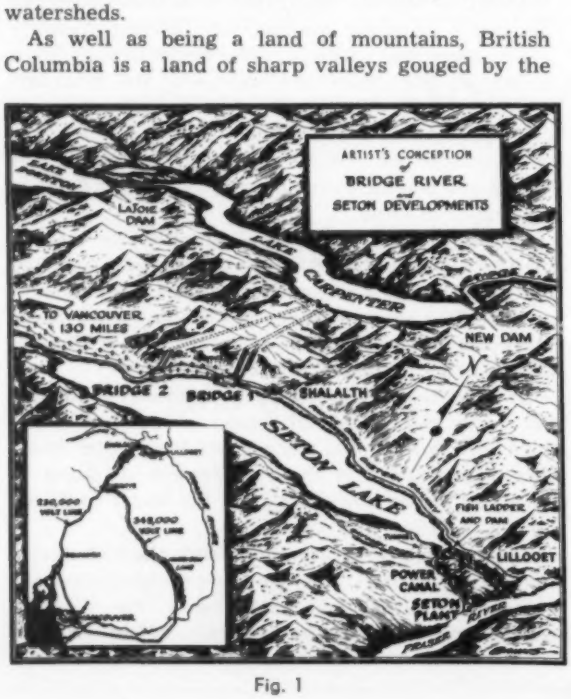

Fig. 1

This technique of diverting water from one watershed to another will permit some spectacular developments in various parts of the province, including the Yukon-Taku, estimated at 4.7 million hp and the Stikine-Liard, estimated at 6-10 million hp, both of these apparently not taken into account in the estimates of the Department of Northern Affairs and National Resources.

The present hydro development in British Columbia totals some 2¾ million hp, concentrated mainly in the south and along the coast.

The undeveloped potential of the various areas in British Columbia is widely dispersed. In general, the province is amply endowed with sites for future hydro development, with only two exceptions—Vancouver Island is rapidly reaching its full development and the Lower Fraser coastal area includes the potential of the Lower Fraser which is a major salmon migratory route. The development of the Lower Fraser presents problems which have not yet been resolved although progress is being made. If the Fraser River is excluded, one must consider this Lower Fraser coastal area as rapidly approaching its full hydro development.

There are four additional areas especially worth comment. The first is the Kitimat-Kemano project of the Aluminum Company of Canada. By damming the Nechako River near the head of the Grand Canyon, a storage reservoir is created impounding the run-off of the Eutsuk-Tetachuck-Euchu and Tahtsa-Whitesail-Ootsa-Netalkuz drainage system, permitting the flow to be reversed through a power tunnel piercing the Coast Range. The area of this watershed is some 5500 square miles.

With the water available and flows approaching 7000 ft³/sec, an estimated 1,718,000 hp can be generated, the installed capacity being 2,214,000 hp in 16 units in the complete development.

The Kenney Dam across the Grand Canyon of the Nechako River is the largest man-made structure in

Canada, some 4 million ft³ of rockfill constituting the dam and supporting on the upstream slope an impervious section of rolled earth enclosed between suitable filter layers. The crest width of the dam is 40 ft, crest length about 1500 ft, and over-all height above bedrock about 320 ft.

The powerhouse is underground. When finally completed it will have installed 16 vertical runners, 4 nozzle impulse turbines, each rated 140-150 thousand hp. Space requirements necessitate a chamber over 1000 ft long, 80 ft wide, and 135 ft high.

The second area especially worth noting is that in the far north of the province on the Yukon boundary, in which is located the complex of lakes and rivers known as the Yukon-Taku power scheme. This project has been surveyed by the Northwest Power Industries project, sponsored by Frobishers Ltd., a subsidiary of Ventures Ltd. Indications were that an early start would be made on phase 1 of the project; then early in 1956, the project was deferred to the future in favor of an earlier start on a 500,000 hp project on the Nass River. The first phase would involve a tunnel four miles above Whitehorse, on the Yukon River; in conjunction with this a one mile tunnel would drain the reservoir into Siliko Lake while a 10 mile tunnel from this lake would drain the water again into a powerhouse on Nakonake River. This development would produce some 660,000 kw. The ultimate development would harness the water power of the Yukon River's intricate system of inland waterways and could be made to generate some 3¼ million kw of electricity or better than 4½ million hp. The scheme is contemplated in conjunction with extensive exploitation of northern British Columbia's mineral resources and the establishment of a large smelting industry, just as the Kitimat project for Al production is based on the hydroelectric energy of the Nechako River.

The third area is the Lower Fraser Coastal. In the western part of southern British Columbia, in that area which is known as the Lower Mainland, the hydro potentials of a number of coastal streams totalling about 1½ milion hp have been largely developed or will be developed within the next five years, principally by the B. C. Electric Company Ltd. Outside of the Fraser River, there remains no water power of a first order in this area to be exploited. The Fraser River could yield 7½ million hp. On the Lower Fraser River some 3 million hp could be developed, in addition to the 1¼ to 1½ million which could be developed at one site alone, known as the Moran Dam site. This Moran Dam would be a dramatic development, rising 720 ft above the present water level and forming a lake 165 miles long; it would be a tremendous asset to the area lying within 150 miles of the bulk of the industries and population of the province. The Fraser River is, however, the principal migratory salmon route in the province and the annual salmon catch originating in the Fraser River and its tributaries is valued at several million dollars. Development of the Moran site might require provision for passing up to ¾ million adult salmon upstream, in a 24 hr period, as well as facilities for the safe passage of migrating fingerlings downstream. In addition to the Moran site there are four sites on the Lower Fraser where low level dams of approximately 100 ft could be built and there are a further six sites on the North Thompson River which flows into the Fraser where low level dams could be built. Again, a fish problem is involved requiring assessment of the possible detrimental effect of a series of dams placed in the path of migrating salmon and requiring solution to the problems which may be involved, although indications are a single low level dam might well be feasible.

The B. C. Electric estimates on the basis of present load growth that the Fraser River or the Columbia, or both, at least in part, will have to be developed within the next 20 years to serve the growing power needs of the area in which it provides service and which today comprises 65% of the population of the province. B. C. Electric is hopeful that techniques can be developed which will allow British Columbia to have the benefit of both fish and power and which will permit hydro development on the Fraser River while at the same time giving the needed protection to the fisheries.

In line with its convictions, on January 4, 1956, the parent company of B. C. Electric, the B. C. Power Corporation, formed a new subsidiary, Western Development and Power Ltd., with two principal functions: (*a*) to develop hydro electric power on the Fraser River to the extent that the maintenance of salmon spawning will allow and on the Columbia River where there is no fish problem, and (*b*) to study industrial opportunities in the areas which can be served with this power and to bring in new industries to use it.

Also in line with its convictions, the directors of B. C. Power Corporation donated $50,000 to the University of British Columbia to make an impartial study of the problem of fish and power on the Fraser River.

The fourth area is the Columbia River. The Columbia River is one of the great drainage basins of this continent, occupying part of British Columbia in Canada, as well as sections of Washington, Idaho, Montana, and Oregon in the United States. The river drains a total of 259,000 square miles of which 40,000 square miles are in British Columbia. However, the water originating in British Columbia accounts for 44% of the average flow of the river and ½ of the 2600 ft drop throughout its 1200 mile length occurs in British Columbia. In the United States 1000 ft of head has been developed to produce some 8 million kw. It is apparent that, although no power has yet been developed in British Columbia, a very large potential does exist.

The river rises in British Columbia in Columbia Lake, then flows northwesterly to the junction of the Rocky Mountain Trench and Selkirk Valley, at which junction, called the Big Bend, the river turns abruptly and flows almost due south. The Mica Creek Dam site is in the vicinity of the Big Bend. This is the principal power site on the Columbia and is only 350 miles from Vancouver, a distance which is within economic transmission of Vancouver at

high voltages in the order of the 345,000 v pressure which B. C. Electric has already pioneered in connection with its Bridge River and Wahleach generating stations.

In addition to the 1½ milion hp from Mica Dam, a further 1 1/3 million hp could be developed at sites at Little Dalles and Priest Rapids and a further ½ million hp on the Lower Columbia River, with sites at the outlet of Arrow Lakes or at the Murphy Creek site further downstream.

Development of the Columbia River sites in Canada hinges on a fair settlement with the United States. It is estimated that the 10 million acre-feet of water which would be stored by the Mica Dam alone would improve the capability of the existing American plants on the Columbia River by some 1.1 million kw. It is quite possible, however, that this water could be used profitably in Canada by diversion to the Fraser and North Thompson Rivers, and engineering studies on the feasibility and economics of such diversion are now nearing completion by the Department of Northern Affairs and National Resources.

In conclusion, mention should be made of the present use of Canadian hydro resources and the prospects for their use in the future. A projection to 1975 made by the Provincial Government indicates a utilization of 12½ million hp, about half the potential of the province. This forecast is certainly a conservative one and anticipates a rate of growth about one-half of that experienced in recent years. A utilization in the order of 16-18 million hp by 1975 may be as likely a figure as 12½ million hp. Nearly one-half of the present turbine capacity of the province is dedicated to the mining industry and it seems reasonable to expect that in future hydro electric development somewhat the same proportion will prevail. The vast northern power resources of the province and of the Yukon are poorly located for general commerce and manufacturing but are ideally located with respect to mineral properties.

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Trends of Electric Power Demands and the Development of Power Resources in Midwest Canada and in Ontario

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This paper gives a general review of the growth in power requirements in midwest Canada and in Ontario and the development of power resources to meet such requirements. Particular reference is made to the area served by The Hydro-Electric Power Commission of Ontario. It is hoped that this paper may give a broader concept of the growth of the power-producing industry and of the steps being taken to assure adequate supplies of electric power as a foundation for the basic economy of these areas.

Planning Power Supply Facilities

The growth and development of electric power has been of fascinating proportions, far greater than was contemplated in the early days when salesmen were employed to go from door to door to convince people that electric lights were superior to gas lights and that electric motors were more effective than steam engines. The main concern of the power supplier in recent years has been to keep abreast of the rapidly increasing need for power by industrial and commercial establishments and by homes and farms.

It is generally recognized that a supplier should have a reasonable reserve of power in order to provide adequate customer service. Reserve power provides for contingencies such as the removal of equipment from service for maintenance purposes, carrying of load in emergencies caused by failure of equipment, etc., and meeting of loads greater than those expected. It is necessary, therefore, that forecasts of service requirements be reviewed continually.

The extension of any organization or enterprise is always based on some estimate of future requirements. The requirements of electrical utilities are almost continuously changing and over a period of years large sums of money are expended in the construction of power plants, transmission lines, transformer stations, and other facilities. It is essential to know that such additions are required and to know when they are needed so that power is available on demand and too early use of capital is avoided. When these two items have been decided, it becomes necessary to determine where such additions should be made, their extent, and character.

Planning is not done on a national scale but rather by electrical utilities and by areas. It is obvious that power demands govern the activities of these utilities. The demand levels in the several categories of load, as well as the rates of growth, vary widely by areas and periods of time. Therefore, an accurate knowledge of past and existing load demands and their characteristics is required. The utility must have not only a good appraisal of its own service area, but a good knowledge of provincial, national, and world economic conditions in order to make a dependable forecast of future growth.

Some of the important factors that must be taken into account when planning the development of power supply facilities, are considered.

First, the electric supply business is a long-range one. There is no development on the horizon—not even atomic energy—that is relegating electric service into obsolescene. The facilities used are inher-

ently long-lived and should be planned, installed, and operated to perform their functions at minimum over-all costs for periods of their useful lives.

Next, the seasonal maxima of power requirements usually determine the amount of peak capacity (kilowatts) required, but it is also necessary to provide for the requisite energy (kilowatt-hours) capacity. Power systems based primarily on hydroelectric generation require a careful consideration of the seasonal variations in the quantity of water available. Likewise, with predominantly fuel-electric systems, careful consideration is given to the availability of types of fuel.

Next is the customer—the most important element in the electric supply picture, since the only reason for having electric systems is to supply customers. The only reason why the business has grown to present proportions is that utilities can convert energy from its raw state—coal, gas, oil, and falling water—into electricity and deliver it in more convenient form, and sell it, with few exceptions, at lower prices than could be attained by the individual customers if they were to undertake providing the service themselves.

Planning, therefore, usually begins with customers. Individually they have distributing systems on their properties and electric operated equipment, the sum total of which measured in kilowatts of absorbing capacity is greater than the productive capacity of the serving utility. The customer, too, is a long-range planner and is either installing, providing for, or changing over to the most modern and useful devices for his business, convenience, or pleasure. To foresee what the future may hold in the greater use of electricity by all classes of customer is the crux in forecasting the demands for power and the physical plant required between the customer and raw energy sources.

To jump from the customer and his requirements to raw energy sources may seem a little out of order, but a finished product cannot be produced without raw material. Alberta, Saskatchewan, Manitoba, and Ontario have in combination large quantities of raw energy resources in the form of coal, oil, gas, water, and the newcomer to the field—uranium. Unfortunately, these resources are not in the backyards of every major center of population. Transportation of large blocks of energy is necessary by some means, in either the raw state or by electric transmission.

Between the customers and raw energy sources comes the power system with its distribution and transmission lines, substations, and power plants. Co-ordinated planning from one end to the other, not the planning of each component separately, is necessary if optimum over-all investments, fixed charges, operating expenses, and service adequacy are to be secured. The task is to search for incremental long-range economies all along the line.

Trends of Power Demands and Development of Power Resources

In June 1955 the Dominion Bureau of Statistics released the first report in a new annual series of statistics relating to the electric power industry in Canada. It contained current and projected data of capability and load for the years 1950-1958 inclusive. The second report in this series, which is now in the process of preparation, will be extended to include the year 1959. The results contained in these reports are compiled from returns filed by 82 producers of electricity, including all of the major privately and publicly operated electrical utilities, and private industries producing substantial quantities of electric power, part of which is usually for sale to the public. The surveys are organized and carried out in cooperation with the Canadian Electrical Association, committees of which are set up to assist in the planning, development, and conduct of these and future surveys.

The results of the second survey are not available at this time. They would be most interesting because

Table I. Gross capability and total demand as of March 1955

	Thousands of kw		
	1950	1954	1958
Alberta			
1. Net generating capability			
(*a*) Hydro	83	202	220
(*b*) Thermal	108	193	393
2. Firm purchases from outside the province	—	4	—
3. Gross capability (1+2)	191	399	613
4. Total demand	179	310	512
5. Difference or indicated reserve (3-4)	12	89	101
6. Indicated reserve expressed as a percentage of total demand	6.7	28.7	19.7
Saskatchewan			
1. Net generating capability			
(*a*) Hydro	85	85	85
(*b*) Thermal	125	239	422
2. Firm purchases from outside the province	—	—	—
3. Gross capability (1+2)	210	324	507
4. Total demand	175	267	369
5. Difference or indicated reserve (3-4)	35	57	138
6. Indicated reserve expressed as a percentage of total demand	20.0	21.3	37.4
Manitoba			
1. Net generating capability			
(*a*) Hydro	421	526	561
(*b*) Thermal	11	51	136
2. Firm purchases from outside the province	68	80	83
3. Gross capability (1+2)	500	657	780
4. Total demand	432	551	679
5. Difference or indicated reserve (3-4)	68	106	101
6. Indicated reserve expressed as a percentage of total demand	15.7	19.2	14.9
Ontario			
1. Net generating capability			
(*a*) Hydro	2349	3463	4062
(*b*) Thermal	127	524	735
2. Firm purchases from outside the province	720	707	666
3. Gross capability (1+2)	3217	4719	5504
4. Total demand	3287	4246	5278
5. Difference or indicated reserve (3-4)	—70	473	226
6. Indicated reserve expressed as a percentage of total demand	—2.1	11.1	4.3

the majority of producers in Alberta, Saskatchewan, Manitoba, and Ontario have raised their sights considerably during the past year in forecasting future power requirements. The results shown in Table I do, however, indicate the manner in which resources are developed to meet load requirements.

Hydro Resources

In the March 1956 release on Water Power Resources of Canada by the Water Resources Branch of the Department of Northern Affairs and National Resources, it was found that:

In Alberta, the larger hydroelectric developments, from which a large part of the southern portion of the province is served, are located on the Bow River and its tributaries. The greater part of water resources is located in the northern half of the province, rather remote from present centers of population.

In Saskatchewan, water power developments are confined principally to mining uses in the northern areas in which water power resources are abundant. The transmission network serving more settled areas is supplied exclusively by fuel-electric plants. Large reserves of coal, oil, and natural gas are located in both Saskatchewan and Alberta; these fuels provide the more economic sources of power in many parts of both provinces, particularly in southern Saskatchewan.

Of the Prairie Provinces, Manitoba has the largest water power resources, there being great potential power on the Saskatchewan, Nelson, and Churchill Rivers. The larger present developments are located on the Winnipeg River and serve Winnipeg, adjacent municipalities, and the transmission network of the Manitoba Power Commission.

Ontario has large water power resources, being exceeded in this respect only by Quebec and British Columbia. It has developed about 57% of its potential water power and ranks second in power generation among the provinces.

With the completion of the St. Lawrence Power project in the International Rapids Section of the St. Lawrence River, the last major hydroelectric site in the southern half of the province of Ontario will have been developed.

In Ontario, about 90% of the total primary energy supplied by central electric stations for consumption in the province is provided by The Hydro-Electric Power Commission of Ontario.

Hydro-Electric Power Commission of Ontario

The Commission, now generally known as Ontario Hydro, was created by the Ontario Legislature following recommendations by advisory commissions appointed in response to public demand that the water power resources of the Province should be conserved and developed for the benefit of all the people of Ontario. In May 1956 it completed its fiftieth year.

The undertaking initially proposed to purchase a block of power from the Ontario Power Company, a private corporation which had promoted and developed the largest single plant on the Canadian side of the Niagara River at Niagara Falls during the period 1902-05, and to transmit this block of power to the municipalities which had signed contracts to take power at cost.

In 1909 the task of constructing a transmission system was begun and by the end of 1910 power was being supplied to several municipalities. At about the same time, a short transmission line and a substation was built to serve a community at the head of Lake Superior, with power purchased from a producer in the vicinity. Today, that part of the Province south of the east-west line drawn through North Bay forms one integrated power network called the Southern Ontario System, while the system west of a north-south line through Sault Ste. Marie is called the Northwestern Division and serves northwestern Ontario.

During the 1930's, Ontario Hydro undertook to operate in trust for the Ontario Government a group of isolated systems serving mainly the mining and pulp and paper industries in northern Ontario. One of these systems was integrated in the Northwestern Division while those remaining were integrated to form the Northeastern Division which since 1950 is interconnected with the Southern Ontario System.

There is no electrical connection at present between the Commission's properties in northwestern and northeastern Ontario.

The tremendous increase in power requirements, together with the fairly recent developments in the field of large-scale power generation and high voltage transmission has advanced considerably the potential value of large capacity regional networks.

Table II. Future primary power requirements, all systems combined, 1956-1980 inclusive

The Hydro-Electric Power Commission of Ontario

Kilowatts

December	(A) Higher estimate	(B) Lower estimate
	Application of 1950-1955 equivalent rate of growth (8.21% per annum)	By Commission's Advisory Committee on Load and Capacity (equivalent rate of growth—5.50% per annum)
1956	4,492,000	4,407,000
1957	4,861,000	4,692,000
1958	5,260,000	4,954,000
1959	5,691,000	5,166,000
1960	6,159,000	5,425,000
	Application to above estimates of 1922-55 equivalent long-term rate of growth (6.56%) per annum)	
1961	6,563,000	5,781,000
1962	6,993,000	6,160,000
1963	7,452,000	6,564,000
1964	7,941,000	6,995,000
1965	8,462,000	7,454,000
1966	9,017,000	7,943,000
1967	9,608,000	8,464,000
1968	10,239,000	9,019,000
1969	10,910,000	9,611,000
1970	11,626,000	10,241,000
1971	12,389,000	10,913,000
1972	13,201,000	11,629,000
1973	14,067,000	12,392,000
1974	14,990,000	13,204,000
1975	15,974,000	14,071,000
1976	17,021,000	14,994,000
1977	18,138,000	15,977,000
1978	19,328,000	17,025,000
1979	20,596,000	18,142,000
1980	21,947,000	19,332,000

Ontario Hydro's long-range studies envisage the interconnection of power resources in northwestern section of the province with those of the northeastern section when the power and economic demands require this final link. This interconnection will tie Ontario Hydro's generating plants into one integrated unit, extending from Quebec on the east to Manitoba on the west, a distance of about 1000 miles. At present the Provinces of Ontario and Quebec and the States of New York and Michigan are interconnected, so it is possible that in the future a vast network of electric power facilities could extend from within the Province of Manitoba in the west into Quebec in the east and from James Bay southward into New York and Michigan.

Customers in the two pioneer systems required in total about 4000 kw in 1910. In 1955 the more than 1-½ million ultimate customers served required more than 4.2 million kw. The requirements were met from 65 hydroelectric and two major fuel-electric generating stations, supplemented by power purchased from other producers.

But what of the future? The Royal Commission, under the chairmanship of Mr. Walter Gordon, which is looking into Canada's economic prospects, has focussed public attention on the future. The many submissions to the Commission from provincial, industrial, and various other bodies have all suggested striking industrial and social developments across the country. Briefs presented by the Ontario Government and by Ontario Hydro's Chairman, Dr. R. L. Hearn, have suggested that, if certain conditions prevail within the province, Ontario Hydro may be faced with loads of the order of 20 million kw by 1980 as compared with just over 4.2 million in 1955.

The two studies which take us to the year 1980 were purely statistical and the figures in Table II are all derived from a projection of past trends. Over the period from 1922 to 1955 the rate of growth for the three operating systems combined has been equivalent to 6.56% per annum and this rate has been applied to two alternative estimates of load in 1960 to give the two projections marked (*A*) and (*B*).

The two estimates for 1960 are 5.4 million or 6.2 million kw. The lower figure has been estimated by the Commission's Advisory Committee on Load and Capacity, a committee charged with the responsibility of preparing five-year forecasts of loads, while the high figure is the load which will have to be met if requirements increase as rapidly as in the period 1950-1955, a rate equivalent to 8.2% per annum. By applying the long-term rate of growth of 6.56% per annum to these 1960 figures, the following kilowatt estimates for the years ahead are reached: 1965, 7.5 or 8.5 million; 1970, 10.2 or 11.6 million; 1975, 14.1 or 16.0 million; and 1980, 19.3 or 21.9 million kw.

The resources required to meet both estimates of load have, of course, been considered, but this discussion is limited to the resources for the higher esti-

Table III. Dependable peak capacity, all systems combined, 1956-1980 inclusive
The Hydro-Electric Power Commission of Ontario

Capacity required to meet higher estimate of future primary power requirements (designated *A*) and provide a margin of reserve of about 7%

Kilowatts

December	Commission's generating stations		Fuel-electric	Power purchased	Total resources
	Hydroelectric	Conventional	Nuclear		
1956	3,258,000	637,000	—	645,000	4,540,000
1957	3,683,000	637,000	—	645,000	4,965,000
1958	4,209,000	826,000	18,000	623,000	5,676,000
1959	4,481,000	1,026,000	18,000	608,000	6,133,000
1960	4,622,000	1,426,000	18,000	608,000	6,674,000
1961	4,717,000	1,726,000	18,000	601,000	7,062,000
1962	4,848,000	2,026,000	18,000	601,000	7,493,000
1963	5,040,000	2,326,000	18,000	601,000	7,985,000
1964	5,052,000	3,039,000	18,000	601,000	8,710,000
1965	5,110,000	3,039,000	418,000	601,000	9,168,000
1966	5,217,000	3,039,000	931,000	601,000	9,788,000
1967	5,250,000	3,339,000	1,131,000	601,000	10,321,000
1968	5,270,000	3,339,000	1,844,000	601,000	11,054,000
1969	5,290,000	3,639,000	2,244,000	601,000	11,774,000
1970	5,333,000	4,239,000	2,644,000	269,000	12,485,000
1971	5,353,000	4,952,000	2,844,000	187,000	13,336,000
1972	5,412,000	5,252,000	3,444,000	187,000	14,295,000
1973	5,442,000	5,852,000	3,757,000	187,000	15,238,000
1974	5,485,000	6,452,000	3,957,000	187,000	16,081,000
1975	5,485,000	7,052,000	4,470,000	187,000	17,194,000
1976	5,485,000	7,765,000	5,070,000	0	18,320,000
1977	5,485,000	8,365,000	5,783,000	0	19,633,000
1978	5,485,000	8,965,000	6,183,000	0	20,633,000
1979	5,485,000	9,565,000	7,096,000	0	22,146,000
1980	5,485,000	10,578,000	7,496,000	0	23,559,000

NOTE: Nuclear resources are based on the assumption that by 1965 nuclear fuel-electric stations will be economical for base load operation.

mates so as to avoid confusion. In 1955 power resources available to the Commission had a dependable peak capacity of more than 4.5 million kw. Table III shows that the capacity required to meet requirements and provide a margin of reserve of about 7% is about 6.7 million kw in 1960; 9.2 million in 1965; 12.5 million in 1970; 17.2 million in 1975; and 23.6 million kw in 1980.

Table III also indicates that between 1956 and 1974 there remain some 2.2 million kw in hydro sites which can be developed economically. Of this amount, more than 1.2 million kw has been authorized for construction and will be in service before 1960. Of the nearly forty economic sites remaining, only six exceed 50,000 kw each. This indicates the main limitation of hydro power in Ontario—there isn't too much left.

One of the more interesting aspects of the study of required capacity is the fact that within a comparatively short period of time Ontario Hydro will start to change over from a predominantly hydroelectric utility to one in which fuel-electric power plays an important part. The rapid developments that are taking place in nuclear studies suggest that after 1965 a large part of the required capacity will be provided by nuclear resources. Nuclear energy will be used to produce steam which in turn will generate electricity in a conventional steam-electric station. Although the 20,000 kw demonstration plant now being constructed near the Des Joachims station on the Ottawa River may not be competitive with conventional fuel stations, it is expected that its operation will provide valuable data for the design, construction, and operation of larger installations. In estimating resources after 1965, it has been assumed that nuclear stations will be economical for base load operation.

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Power from Other Energy Sources

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Brief comment on thermally produced power obtained from the burning of natural mineral fuels, coal, oil, and gas, is given. Currently, the energy of these fuels is the only accepted alternative to hydro energy for producing commercial electricity in quantity, and, by and large, the bulk of electric power produced in the world, with a few nations excepted, is produced by the combustion of these fuels in steam plants of more or less conventional design.

Power from Nuclear Energy

It is now recognized that nuclear energy released through the fission process is an impending source of high-level controlled heat. As such it becomes a fourth fuel which, if proven economic to produce, safe to handle, and reliable in operation, not only has strategic advantages, but is a much larger resource on a world basis than the combined reserves of our conventional fuels.

Admittedly, if heat is generated, power can be produced in the same way as from conventional fuels, but many obstacles have yet to be overcome before competitive atomic power is a reality. Its commercial development, other than in the prototype and proving stages, is not likely in Canada for a decade or more.

The elementary concept being developed concedes that the only part of the electrical process affected is the means for producing steam; conventional boiler steam is replaced by steam produced by an atomic reactor. The turbine and generator, with ancillaries on both the prime mover and electrical sides, remain relatively the same. However, initially, there are two fundamental differences worthy of note. First, the atomic reactor costs more than the boiler it replaces. Second, atomic steam will be of relatively low pressure and temperature in comparison with the best steam cycles serving conventional steam-electric plants. Consequently, the efficiency of the conversion will be lower and the corresponding heat rate higher. Badly needed metallurgical improvement in components to withstand higher heat, pressure, and rotative forces would benefit both the atomic and conventional steam cycles. In fact, the eventual competitive success of the atomic power cycles may well depend on such improvements being made.

It would appear that the main benefit to accrue from the fission process rests on the possibility of obtaining extremely low fuel cost, variously estimated at from less than one to several mills/kwhr of power produced. Even though it be granted that the fuel cost is extremely low, the margin of cost between it and conventional fuel must be wide enough to warrant any increased capital expenditure. Low fuel cost, be it one mill or two, is offset in part, if not in whole, if greater fixed charges are necessitated by the complications and dangers of the fission process.

Viewed from the economic standpoint, atomic power can be regarded at present only as a possible supplement to power resources in very high-cost, energy-deficient areas. Also, Canada could not seemingly derive any particular advantage over

other countries since, presumably, the cost of power from nuclear fission will be approximately the same regardless of plant location.

On the economic side, the following press statements attributed to power authorities are of interest:

(*A*) Mr. J. A. Fuller, President, Shawinigan Water and Power Company, *Financial Post*, March 21/55: "I think it can be said that atomic power will supplement but not supplant our conventional power sources, at least so long as our supply of fossil fuels (coal, oil, and gas) holds out. . .

"It will never displace presently developed hydro power nor in fact future hydro power which can be sold near the site of development or transmitted over feasible distances."

(*B*) Sir John Cockcroft, Director, Atomic Energy Research Establishment, Harwell, England, *Ottawa Citizen, C. P.*, April 2/56: "Sir John says he sees little likelihood of any widespread use of atomic power in countries like Canada where abundant hydro-electric resources exist. 'Hydro-electric resources can provide power much more cheaply than nuclear energy'. . ."

Thermal Electric Power Outlook

In Canada, when power comes to mind, one quite naturally thinks of hydroelectric power derived from the force of falling water. This is so because, with the single exception of Norway, the Canadian per capita production of electricity from water power leads the world. Hydro generation furnishes about 95% of the electricity produced in Canada. It also accounts for as much as 10% of Canada's present energy consumption for all purposes, a figure that is approached by few nations. Only three countries, United States, Russia, and United Kingdom, each with from 3 to 14 times Canada's population, produce more electric power on a volume basis, and this mostly from coal-fired steam plants.

In consequence, the average Canadian has become very "hydro-minded," and has certain fixed ideas, if not real prejudices in favor of the relative importance of hydro vs. thermal electric power. He is firmly convinced that hydro power is cheap and all thermal power must be dear. In his opinion steam-electric power is outmoded, and positively antiquated if it must be produced from coal. This average Canadian does not fully realize that his electrical requirements are rising faster than the ability of hydro to provide power on economic grounds. Neither does he realize that the total known hydro potential available for his use is very small, less than 1/10 of 1% in relation to Canada's potentially available reserves in coal, oil, and natural gas. Nor does he fully appreciate the insatiable world demand for the products of the vast Canadian stores of forest and mineral wealth, a demand created by two world wars, and the threat of a third, a demand which can be satisfied only by gigantic expenditures of energy fast outpacing any past rate of use. This gives rise to speculation, in no small degree, in regard to the relative importance of hydraulic energy and thermal energy in a future economy. While both are important, the latter for obvious reasons becomes increasingly so as load requirements develop.

Table I. Canada's available energy reserves from conventional sources. Estimated Dec. 31, 1955, in millions of net tons of equivalent coal (24 million Btu/ton)

Source	Type	Amount	% of Total
Coal	Expendable	98,816	98.3
Natural gas	Expendable	875	0.9
Crude oil*	Expendable	726	0.7
Water power	Renewable	58	0.1
	Total	100,475	100.0

* Exclusive of potential in tar sands and oil shales.

Canada's Energy Reserves

Canada's increasing population, its desire for ever-higher living standards, the changes in outlook and technology that have taken place during and since World War II are mainly responsible for the present great concern with energy reserves. Since 1950, that concern has been expressed widely in print. There have been several book-length surveys, literally hundreds of technical papers, and an untold number of popular articles and published discourses on every phase of energy assessment. Taken with the popular and vociferous outcry for atomic power, and the benefits it in particular is expected to bring, one must almost conclude that the world, and every country in it, is shortly to be faced with an energy crisis. Can this possibly be true for Canada?

First look at an estimate of Canada's reserves, as given in Table I.

It should be noted that in this and subsequent tables the estimates for coal and oil are calculated from somewhat different bases. Oil reserves are computed from recovery estimates of a high degree of reliability. Coal reserves, although subject to a recovery factor, still remain mostly reserves computed from geological evidence rather than from mining evidence.

Recoverable reserves of conventional energy at the end of 1955 were estimated to be of about the following order: 99 billion tons of mineable coal; 3 billion barrels of recoverable crude oil; 21 trillion ft^3 of natural gas; and 66 million hp of hydraulic power, truly a remarkable conglomeration of figures.

To assess these figures on a comparable basis, a common unit that is readily understood must be adopted. If stated in ordinary units of hp-hr, kwhr, or Btu's, the figures become so enormous as to be almost beyond understanding. Therefore, the author presents the reserves in terms of one million tons of equivalent coal with a heat content of 12,000 Btu/lb; first, because it is easier to visualize what a ton of coal looks like than a single Btu, kwhr, or hp-hr; second, because this large unit aids comparison and simplifies tabulation.

As an indication of the size of this unit, one million tons of such coal, used at the average 1954 operating efficiency of American steam-electric generating plants, would produce two billion kwhr of electricity. As few as 35 of these units would produce Canada's total 1954 electrical output.

Table II. Geographic distribution of Canada's energy reserves. Estimated as of Dec. 31, 1955, in millions of net tons of equivalent coal (24 million Btu/ton)

Region	Amount	% of Total	Percentage from Coal	Oil	Gas	Hydro
Alberta	49,201	49.0	97.3	1.3	1.4	*
Saskatchewan	24,246	24.1	99.5	0.3	0.2	*
British Columbia	18,988	18.9	99.2	*	0.8	*
Yukon & N. W. T.	4,521	4.5	99.8	0.2	—	*
Nova Scotia	3,115	3.1	100.0	—	—	*
Ontario	159	0.2	94.5	0.3	*	5.2
Manitoba	117	0.1	86.5	8.1	*	5.5
New Brunswick	102	0.1	99.6	*	*	0.4
Quebec	23	*	—	—	—	100.0
Newfoundland	3	*	—	—	—	100.0
Prince Edward Island	*	*	—	—	—	100.0
Canada	100,475	100.0	98.3	0.9	0.7	0.1

* Negligible amount of total.

Here it will be noted that, of the energy sources shown, coal is by far the most abundant. While water power is shown to be only a small fraction of the total, its importance in Canada's economy is much greater than this comparison suggests, because of its availability and its renewable characteristic in the otherwise energy-deficient area of the "St. Lawrence Lowlands." This relatively small area supports as much as 60% of Canada's total population and the bulk of the secondary industries, and requires, with minor exception, import of all its fuel energy either from distant points in Canada or the United States. On the other hand, proven oil and gas reserves in Canada, although not large in comparison with coal, are increasing at a phenomenal rate. One authority has recently estimated that in 1980 proven oil reserves will be about 5 times greater than they are today.

Table II shows the geographic distribution of reserves. Here it will be noted that over 96% of these reserves are located west of the Manitoba-Saskatchewan border, and of the remaining 4% at least 3 are in Nova Scotia. The table shows also that coal is preponderantly the greatest reserve in 8 of the 11 specified regions, with hydraulic power the only energy source in the remaining three.

Table III. 1954 Production of energy in Canada. In millions of net tons of equivalent coal (24 million Btu/ton)

Region	Amount	% of Total	Percentage from Coal	Oil	Gas	Hydro
Alberta	30.7	58.4	15.8	69.2	14.6	0.4
Nova Scotia	5.9	11.2	98.7	—	—	1.3
Quebec	4.9	9.3	—	—	—	100.0
Saskatchewan	3.7	7.0	58.0	35.9	3.9	2.2
Ontario	3.4	6.5	—	3.0	12.4	84.6
British Columbia	2.0	3.8	63.4	—	—	36.6
Manitoba	1.0	1.9	—	54.9	—	45.1
New Brunswick	0.9	1.7	88.2	0.3	0.9	10.6
Yukon & N. W. T.	0.1	0.2	13.7	85.2	1.1	*
Newfoundland	*	*	—	—	—	100.0
Prince Edward Island	*	*	—	—	—	100.0
Canada	52.6†	100.0	28.4	44.2	9.6	17.8

* Negligible amount of total.
† Approximately 1900 years supply at this rate and with present reserves.

Table IV. 1954 Total energy made available for use in Canada. In millions of net tons of equivalent coal (24 million Btu/ton)

Source	Amount	% of Total
Crude oil	50	50.5
Coal	34	34.3
Water power	10	10.1
Natural gas	5	5.1
Total	99*	100.0

* Approximately 1000 years supply at 1954 rate of use.

Table III shows the 1954 production from Canada's reserves. Here it is seen that as much as 71% of the 1954 production of primary energy was produced in Western Canada, with the province of Alberta contributing over 58% of the total. Nova Scotia was second with about 11% of the total. In only 4 of the 11 specified regions did coal lead. Oil led in 3 and hydraulic power in the remaining 4. It should be noted that, at the rate of production shown, Canada's present reserves are sufficient for a minimum of 1900 years.

Table IV gives an approximation of the energy consumed in 1954.

Remembering, as shown in Table III, that Canada's production is 52.6 units of energy and its consumption, as shown in Table IV, is approximately 99 units, it is apparent that Canada is dependent on import for about one-half of its energy requirements, mostly in the form of coal and oil. It is also apparent that oil leads coal by a considerable margin, a reversal of position which has developed very recently owing in no small measure to the phenomenal advance in production from indigenous oil reserves. It is further apparent that present Canadian energy reserves are sufficient to support the current rate of use for a minimum of 1000 years and, in the case of a fourfold increase, as has been forecast by some, for something in excess of 250 years. Consequently, there is no danger of an energy shortage from conventional sources for a long time. Some of the energy reserve may be badly placed, but at the least, it is available for use if, as, and when required. Moreover, there is every assurance that more energy, particularly in the form of oil and gas, will be found to supplement present reserves, and extend their life even beyond the times here forecast.

Development of Thermal-Electric Power

Fig. 1 and 2 and Table V give a view of the history and of the progress attained in using heat-activated motive force in the production of electricity.

Fig. 1 illustrates successive time stages in the method of converting fuel energy to power, and the corresponding practical efficiencies obtained from various types of prime mover. At present, the steam turbine outranks all other heat engines in size and performance for powering central generating plants. In the United States, station heat rates of well under 10,000 Btu/net kwhr have been reached, with efficiencies of 37-38%. New units under construc-

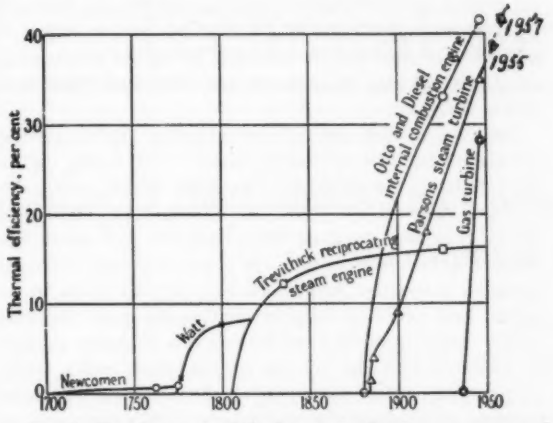

Fig. 1. Development of fuel energized prime movers and corresponding plant efficiencies, 1700-1950. From "Revolution in Fuel Technology," by M. W. Thring, Journal of the Institute of Fuel, Vol. XXVII, No. 163, Aug. 1954.

tion, employing advanced steam cycles with supercritical pressures as high as 5000 psi, temperatures to 1200°F, and double-stage reheat, are expected to raise efficiency for condensing plants by as much as 3-4%. Turbo-generator size has reached 250,000-kw capacity; 325,000-kw capacity machines are being built, and 400,000- to 500,000-kw sets are regarded as possible.

Fig. 2 illustrates the progressive improvement in the efficient use of fuel. One pound of coal, or its equivalent in oil or natural gas, now develops as much electricity as did 3 lb in 1920, and as did 10 lb when the Central Electric Station Industry came into being in the last quarter of the 19th Century.

Table V shows the present average conditions applying to steam-electric generating plants operating in Canada, and comparable conditions for the United States and the United Kingdom. These data speak for themselves and require little comment. However, it should be noted that the averages given in respect to performance and economy are far below the best attainable from the most advanced plants. Canada suffers in the comparison, largely because of the amount of capacity held in reserve, the preponderance of small generating units, and over-all

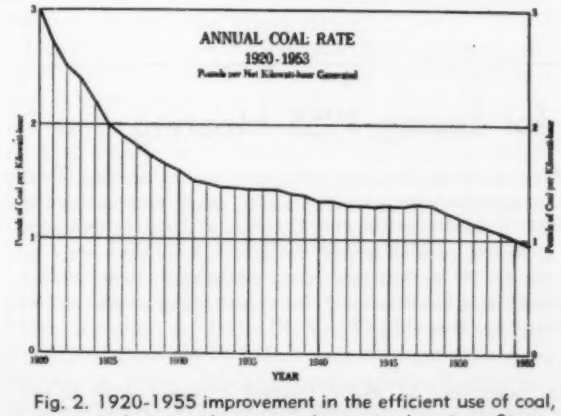

Fig. 2. 1920-1955 improvement in the efficient use of coal, or its equivalent in oil or natural gas, in American Steam-Electric Utility Plants. Adapted from 34th Annual Report 1954, U. S. Federal Power Commission.

Table V. 1954 Comparative data for steam-electric generating plant. Operated by The Central Electric Station Industry

	Canada	United States	B.E.A.* United Kingdom
Production, 10^9 kwhr	3,144	360,973	61,658
% (of thermal generation	93	99	100
(of total generation	5	77	99
Capacity, 10^3 kw	1,551	74,773	—
% (of thermal capacity	92	97	—
(of total capacity	12	75	—
Weighted Average	†		
Heat in coal used, Btu/lb	10,660	12,180	10,792
Heat rate, Btu/net kwhr	15,555	12,180	14,580
Coal rate, lb/net kwhr	1.459	1.000	1.352
Thermal efficiency, %	21.9	28.0	23.4
Price of coal/net ton, $	7.08	6.25	7.88
Cost of fuel/million Btu, ¢	33.2	25.7	36.6
Fuel cost/net kwhr, ¢	0.443	0.300	0.494

* British Electricity Authority, Sixth Annual Report, year ending March 31, 1954.
† Canadian averages are based on 24 of the largest steam-electric stations. In 1954, these 24 operations accounted for over 90% of the capacity and production from the 168 thermal plants controlled by the industry.

operation at very low load factor, all of which militate against the most efficient performance.

Table VI gives a projection of the amounts and types of electrical generating capacity that will be needed between 1951 and 1981. It has been said that "people would rather be misinformed about the future than correctly informed about the past." If this be true, a forecast of the power trend would seem to be in order at this point. This projection, the counterpart of several all showing similarity in regard to over-all amounts, has been selected because of its bold attempt to delineate the type as well as the amount of operating capacity at five-year intervals, a quarter of a century into the future. Here it is indicated that hydroelectric power will remain Canada's principal source of electrical energy for at least the next 25 years. At that time, it will possibly represent as much as 2/3 of the total. In the meantime, thermal capacity will have become increasingly important and will have risen from a quite minor position in 1951 to about 30% of the total by 1981.

Table VII, in another way, attempts to show the past and future growth trend of thermal vs. hydrogenerating capacity. In the 10-yr period prior to the end of the war, thermal power had a growth rate and total capacity less than hydro power. In the

Table VI. Projected electrical capacity in Canada 1951-1981*. In millions of kilowatts

Year	Total	Hydro	Thermal		
			Total	Coal, oil, gas	Nuclear fuel
1951	11.1	10.0	1.1	1.1	nil
1956	16.0	14.0	2.0	2.0	nil
1961	22.5	20.0	2.5	2.4-2.3	0.1-0.2
1966	28.0	24.5	3.9	3.7-2.9	0.2-1.0
1971	34.0	27.4	6.6	6.0-4.9	0.6-1.7
1976	41.0	30.2	10.8	8.8-7.5	2.0-3.3
1981	48.0	33.0	15.0	11.0-8.0	4.0-7.0

* Source—Unclassified A.E.C.L. Paper No. 210 presented at Geneva, Switzerland, Aug. 1955 by Messrs. Davis and Lewis.

Table VII. Growth trend of thermal vs. hydro electric capacity. Expressed in annual (compound) percentage and by ratio

Interval	Period	Thermal	Hydro	Ratio thermal to hydro
10 years	1935-45	2%	3%	1:15
10 years	1945-55	14%	6%	1:7
Projected 30 years*	1951-81	9%	4%	1:2

* Calculated from data taken from unclassified A.E.C.L. paper No. 210 presented at Geneva, Switzerland, Aug. 1955 by Messrs. Davis and Lewis.

10-yr period after the war, the growth rate of thermal power was more than double that of hydro, and quantitatively had halved the former capacity ratio of 1:15. Projection in the 30-yr period 1951-1981 indicates that the accelerated growth rate for thermal capacity will continue at about the same differential, and that, quantitatively, the ratio between thermal and hydro capacity will narrow to a ratio of as little as 1:2.

Conclusion

From present indications it is evident that most progress in the use of thermally generated power is developing in three main regions, viz., the Maritimes, southern Ontario, and the Prairie Provinces. In these regions it is anticipated that the power demands within the next 25 years will far surpass the supply of economically available hydraulic energy. Therefore, from now on, it can be reasonably expected that thermal power will be called on to play an increasingly important role in the Canadian power picture.

Because of the location of existing fuel supplies, development will probably follow some fairly definable pattern. In Western Canada, where coal, oil, and gas reserves are most abundant, these fuels will likely continue to give the cheapest and most dependable thermal power. In fuel-deficient Central Canada, imported American coal would seem to be in the best position to provide the cheapest thermal power until nuclear fuel becomes a cheaper source. In Eastern Canada, where highest fuel costs apply at present, indigenous coal and imported oil have become increasingly competitive, and either one or the other, depending on circumstances, will produce the cheapest thermal power until nuclear fuel gains the hoped-for advantage at some time as yet unknown. Meanwhile, Canada is indeed fortunate in being endowed with such abundant fuel resources with which to meet the indicated growing demand for thermally generated electric power.

Manuscript received Oct. 2, 1956. This paper was prepared for delivery before the Ontario-Quebec Section of the Society, May 11, 1956.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1958 JOURNAL.

Manuscripts and Abstracts for Spring 1958 Meeting

Papers are now being solicited for the Spring 1958 Meeting of the Society, to be held at the Statler Hotel in New York City, April 27, 28, 29, 30, and May 1, 1958. Technical Sessions probably will be scheduled on Electric Insulation, Electronics, Electrothermics and Metallurgy, Industrial Electrolytics, and Theoretical Electrochemistry.

To be considered for this meeting, triplicate copies of abstracts *(not to exceed 75 words in length)* must be received at Society Headquarters, 1860 Broadway, New York 23, N. Y., *not later than January 2, 1958. Please indicate on abstract for which Division's symposium the paper is to be scheduled.* Complete manuscripts should be sent to the Managing Editor of the JOURNAL at 1860 Broadway, New York 23, N. Y.

* * *

The Fall 1958 Meeting will be held in Ottawa, Canada, September 28, 29, 30, October 1, and 2, 1958, at the Chateau Laurier.

Technical Review

Report of the Chlor-Alkali Committee of the Industrial Electrolytic Division for the Year 1956

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and

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For over a decade each succeeding year has marked a new production record for Cl and caustic soda. The year 1956 was no exception with Cl hitting an all-time high of 3.78 million tons, an increase of 11% over 1955. Caustic soda production likewise established a record in 1956 reaching 4.21 million tons, an 8% increase over 1955. Lime-soda caustic represented about 11% of the total, with the remainder being electrolytic caustic.

The chlor-alkali industry has grown so large that its power requirement in 1956 is estimated to have been over 12 billion kwhr. This is about 2% of the total electrical energy output of the nation.

Caustic potash is being looked upon with greater interest by the chlor-alkali producers. The production in 1956 was 92,000 tons on an 88-92% KOH basis. During the year Diamond Alkali started producing caustic potash at Muscle Shoals, as did Pennsalt Chemicals at Calvert City.

Sodium chlorate production in 1956 was 55,000 tons, up 11.8% over 1955.

The Cl growth rate averaged about 12% annually for many years. Although there are indications of a lower growth rate in the production figures for the last 5 or 6 years, the forecasters predict an impressive 10% increase in 1957. This new demand will be adequately met with new plants and expansion programs now under construction.

Caustic soda has experienced a steady growth rate of about 7% annually over many years, and this rate is expected to continue for at least 5-10 years. In 1955 Dow started producing soda ash from electrolytic caustic at its Freeport, Texas, plant. Other producers are known to be preparing themselves for this means of solving their excess caustic problem.

Markets and End-Use Patterns

There were no outstanding changes in the markets and end-use patterns for Cl and caustic during 1956. Chlorine requirements for $TiCl_4$ increased because the growing Ti metal industry doubled production in 1956. The pulp and paper industry required more of both Cl and caustic. Other Cl-consuming industries showing growth during 1956 were plastics, chlorinated solvents, agricultural chemicals, and textiles. Chlorine also continues to be a growing workhorse in its role as an intermediate in the production of chemicals.

Process changes do occur in which a Cl-consuming process may be modified or substituted for, and thus eliminate the need for Cl. For example, C_2H_4O is now made by direct oxidation in preference to the Cl-consuming chlorohydrin process, and some phenol is made by the cumene process instead of the long-practiced chlorobenzene route. No process changes of this type, however, occurred during 1956.

Caustic soda is enjoying its growth in (*a*) metal ore digestion, (*b*) development of cold caustic pulping in the paper industry, (*c*) petroleum, (*d*) textiles, and (*e*) chemical manufacture. The Al industry is expanding and the increased alumina production requires more alkali. A trend in this industry is the increasing use of electrolytic caustic instead of soda ash to supply alkali requirements.

The year 1956 found an increasing number of small chlor-alkali plants being built in foreign countries. Our caustic exports may decrease as these foreign plants are put into operation to supply local demands. Consequently, a decrease in caustic exports will make it more difficult for some companies to dispose of excess caustic.

Table I.[1]

Cl		Caustic soda	
	%		%
Pulp and paper	15.0	Chemicals	26.9
Chlorinated solvents	13.0	Rayon and film	17.8
Automotive fluids	11.0	Pulp and paper	6.6
Plastics and resins	11.0	Exports	5.9
Insecticides, herbicides	7.5	Petroleum refining	5.5
Refrigerants, propellants	5.0	Lye and cleansers	4.1
Water and sewage	3.5	Textiles	3.5
Others	34.0	Soap	2.1
		Others	27.6
	100.0		100.0

[1] Source, *Chemical Week*, May 26, 1956.

Table I shows the approximate end-use patterns for Cl and caustic soda.[1]

Announcements of New Plants and Expansions—Current to May 1957

Kaiser Aluminum & Chemical Corp.'s 36,000-ton/yr Cl—40,000-ton/yr caustic plant now under construction at Gramercy, La., will go into production this year. This marks the first entry of an U. S. aluminum company into the chlor-alkali field. The caustic will be used in the company's adjoining alumina plant. Diaphragm cells of the Hooker S3B type will be installed.

Dow Chemical is another chlor-alkali producer favoring Louisiana with a new facility. The company is building a plant at Plaquemine to produce Cl and caustic and a number of organic chemicals.

Wyandotte Chemical Corp. also selected Louisiana for a Cl and caustic plant to be built at Geismar. Contracts for design and construction of the diaphragm cell plant have already been awarded. This new 300-ton/day chlorine and 350-ton/day caustic plant increases Wyandotte's capacity by over 50% and represents their first move away from Michigan and into the South.

Jefferson Chemical Co., a large consumer of Cl, is in the planning stages of a new diaphragm cell plant to be located in Port Neches, Texas.

The Solvay Process Division of Allied Chemical & Dye Co. has built a new Hg cell plant at Brunswick, Ga. Before the plant was completed, the company announced plans to double the initially planned capacity. The additional capacity is expected to be in operation by this fall, making a total daily output of about 200 tons of Cl and 250 tons of caustic.

Weyerhaeuser Timber Co.'s new Cl plant at Longview, Wash., started operation December 1, 1956. Initial capacity is 80 tons/day, with provision for doubling in the near future. This is the largest captive Cl plant in the paper industry. It employs the new De Nora 14TGL cell.

Expansions of existing chlor-alkali plants are also very much in the news. Columbia Southern is expanding at Lake Charles, La. Frontier Chemical Division of Union Chemical & Materials Corp. announced expansion plans at both Denver City, Texas, and Wichita, Kan., to make a total production of about 225 tons/day of Cl. At Calvert City, Ky., Pennsalt Chemicals Corp. announced an expansion scheduled to go into operation during 1957 to increase Cl production from 50 to 150 tons/day.

Olin-Mathieson's subsidiary is expanding its McIntosh, Ala., plant to 250 tons/day of Cl; completion was scheduled for the early part of this year.

At Deer Park, Texas, Diamond Alkali is building a Hg cell plant to operate in combination with an existing diaphragm cell plant. The added facilities are scheduled to be in operation during the first half of 1958. The addition will increase daily production at Deer Park by approximately 40%, or 200 tons of Cl and 220 tons of caustic.

Westvaco Chemical Division of Food Machinery & Chemical Co. is in the middle of a complete overhaul of their 460-ton Cl plant at South Charleston, W. Va. The first circuit of Hooker S3B cells went on the line in March 1957.

Du Pont recently announced a multimillion dollar expansion at its Memphis, Tenn., plant to produce Cl and Na metal. The expansion will represent an increase of better than 50% in Du Pont's Na capacity.

Dow Chemical Co. of Canada, Ltd., announced an increase in facilities at Sarnia. Early in 1956 it was announced that Shawinigan Chemicals, Ltd., would build a new chlorine-caustic plant at Shawinigan Falls. In British Columbia, Hooker Chemicals of Vancouver, Ltd., has a large chlorine-caustic plant under construction, scheduled for completion in June 1957. This is the first plant of this type in Western Canada, and employs the S3B cell now rated at 30,000 amp instead of 25,000 amp.

The Oldbury Division of the Hooker Electrochemical Co. is expanding an existing $NaClO_3$ plant at Columbus, Miss., to bring total capacity to 22,000 tons/yr.

The American Potash & Chemical Corp. is coming East, having announced a new $NaClO_3$ plant to be constructed on a 586-acre site on the Tombigbee River about 8 miles south of Aberdeen, Miss. The plant, scheduled for completion in mid-1958, will have an initial capacity of 15,000 ton/yr.

Technical and Outstanding Commercial Developments

A pioneering step to convert a-c to d-c power for a chlor-alkali plant is being taken by Diamond Alkali in their multimillion dollar expansion program at Deer Park, Texas. The company plans to install the world's largest Ge rectifier system instead of the normally used Hg arc or mechanical rectifiers.

A new De Nora development is a high capacity Hg cell design on which the company has been working for several years. The cell, referred to as the SGL type, has a rated capacity of 120,000 amp, but is reported to be capable of operating at a still higher amperage. The first major application of this cell in this country will be Diamond Alkali's installation of 52 cells at Deer Park, Texas.

A patent has been granted to the Hooker Electrochemical Co. for the recovery of dilute Cl gas. The process is based on the preferential absorption of Cl into water at high pressure. The company offers to make the process available to the industry on a license basis.

Manuscript received May 22, 1957. This paper was prepared for delivery at the Washington Meeting, May 12 to 16, 1957.

Any discussion of this paper will appear in a Discussion Section to be published in the June 1958 JOURNAL.

Feature Section

The Materials Problem in Relation to Our Society

Presidential Address*

Hans Thurnauer

It has been a great privilege for me to serve as your President. If I were to call the names of those who have served our Society during the year, it would take the major part of my time. I would like to take this opportunity, however, to thank you, one and all, for your unselfish services which made this, I feel, a successful year. We already have discussed the status of our Society at the annual business meeting, but I would like to make a few remarks at this time.

Although we are not large in comparison to some other technical societies, our many activities make our administration quite complex. Nevertheless, we are able to keep a smoothly running organization, thanks to the devotion of many active members to their assigned duties, and thanks to our fine office staff in New York.

We are known as a friendly society. I felt it personally during the year while visiting some of our local sections, and all of us notice it at the national conventions.

And we are growing, not only in numbers but also in the scope of our activities.

One significant sign of this is the fact that we have outgrown our headquarters in New York. We have acquired new office space at 1860 Broadway, near Columbus Circle, which is a far better location than the former one, but we are still actively looking for a permanent location. Eventually we may obtain space in a proposed new Engineering Societies Building in New York which will be ready in a few years. To gauge our need of office space and also to allow room for expansion, we were asked during the year to estimate our needs for the next 5, 10, 25, and even 50 years. While, admittedly, this is not unreasonable to ask, it certainly is not easy to answer. Now, if the President finds himself in difficulties of this sort, he usually forms a new committee (I guess this is the reason we have so many committees), but since an early reply was necessary, I consulted with our able Secretary, Dr. Linford. He made some quick mental computations and came up with a "guesstimate," which seemed to be quite satisfactory for the intended purpose.

I mention this here because it brings to my mind the question of the Society's growth. Dr. Hunter, on the occasion of our 50th Anniversary in Philadelphia, entitled his address "The Electrochemical Society, Past and Future." He eloquently described the past 50 years, but with the typical restraint of the scientist, made the following statement about our future: "It may be necessary for you to wait for your 75th Anniversary President to obtain the long-range planning; however, I do believe that the future should be interesting." I am sure that this noncontroversial statement, "that the future should be interesting," is all that could be said about it, either now or then. Fortunately this is only our 55th Anniversary and not our 75th, and so I am not obliged to out-guess Dr. Hunter. I think that he was very wise in not predicting the utopia of technical achievements about which we read and hear so much these days. The accelerated pace in research and development makes it practically impossible to make reliable predictions, conservative or otherwise.

Let us look first at the conservative side. Recently Dr. Lee deForest, the eminent radio pioneer, spoke on a similar subject. Based on the limitations of material capabilities, as we know them today, he doubted that man would fly to the moon in the foreseeable future. This statement was based on facts and, yet, quite a few people probably regard it as heresy.

On the other hand, consider just a few of the recent technical accomplishments which make us wonder whether we are not actually closer to seemingly impossible achievements. How many dared to foresee, just a few years ago, that man would be able to fly several times faster than sound? Could any physical scientist have predicted with certainty only five years ago that synthetic diamonds could be made, or other synthetic materials even harder and more temperature-resistant than diamonds?

And yet, these strikingly new technical developments are realities today. They came about through improvements of materials, or better and novel processing of known materials. We, the members of The Electrochemical Society, are essentially a group of "Material Scientists," and therefore deeply involved and interested in the problem of creating new materials. For this reason I have chosen to discuss "The Materials Problem in Relation to our Society."

I consider it axiomatic that all technical progress goes hand in hand with the availability and usage of better materials. Many examples of the validity of this statement can be cited. The electric light bulb's performance was radically changed by switching from a carbon filament to tungsten, a seemingly simple improvement. The development of light-weight aluminum and its alloys made powered flight practical. The development of high-temperature, high-strength alloys made the gas turbine a useful and practical power plant. Production of extremely pure silicon or germanium made transistors possible.

But now we have set our sights on new technological achievements which pose far more difficult problems than any thus far encountered. They comprise practically all fields of scientific endeavors. The necessity of maintaining our military superiority demands that we build ever-faster and farther-reaching planes or missiles,

* Delivered at the Washington Meeting, May 14, 1957.

and more powerful weapons. Conservation of our natural resources, and our dependence on a number of foreign raw materials, necessitate the search for new energy sources and substitutes for scarce and hard-to-get raw materials.

Physicists have shown us that the goals which we have set for ourselves are on a sound basis, but we lack materials to withstand the new environmental conditions with which we must cope. Among these are extremely high temperatures, nuclear radiation, high intensity sound, high energy shock, and vibration over a broad frequency band, to name just a few. Material development has become the Achilles' heel of our technological advance.

This is a problem of deep concern to all who are interested in a very broad spectrum of materials. I am tempted to state that it is closely related to the future of our Society and, in a broader sense, to the future of our nation. It is an appropriate subject for this particular meeting here in Washington where so many decisions are made, which in the final analysis hinge upon the availability of suitable materials.

Past performance proves that electrochemistry has made substantial contributions to material development. Perhaps, someday, an ambitious economist among us will reduce to figures all the benefits which our members have brought to the economy as a whole by creating new materials and processes to produce them. The technical program of this convention and the papers published in the JOURNAL attest to the fact that we are keenly aware of the materials problem as it exists at present. Herein lies the strength of our Society and the fulfillment of our obligation to our nation.

At the risk of omitting many important examples of our interest in materials research, I would like to cite just a few instances of contributions with which I am more familiar and which are of particular consequence to the National Defense effort.

We are very active in the field of high-temperature materials, both metallic and nonmetallic. Silicon carbide and graphite, the old work horses of electrochemical technology, are materials of extreme importance today to rocket and guided missile development. Other refractory carbides, also borides, nitrides, and silicides, are under intense investigation because of their extremely high melting temperatures and hardness. They are being considered for materials of construction in rocket nozzles and similar applications where high temperature and erosion resistance must be combined.

Our interest in rare metals, actually as old as the Society itself, is reaping rewards at present and will become still more important in years to come. Their usefulness as high-temperature materials, also in electronic and atomic applications, has been assured.

Further, we are interested in materials for communication systems, one of the major factors in modern warfare. An increasingly broader frequency band is put to use to accommodate the innumerable electronic devices for modern defense and attack systems. For this reason our studies of electrical insulators, semiconductors, and capacitor dielectrics are of vital importance to the Armed Forces who must be able to operate electronic gear under the most adverse conditions of temperature, pressure, and humidity.

In the battery field our members acquire and furnish useful information toward the development of more compact and reliable batteries, mostly for military applications.

Our Society has pioneered in corrosion studies and our members supply to corrosion problems the fundamental knowledge which, for instance, helps our Navy prevent marine corrosion.

Contributions of other members make it possible to produce light metals for plane structures, such as aluminum, magnesium, titanium, and, lately, beryllium.

We, as a Society, also have recognized that basic research is the key to new materials development and we look to the members of our Theoretical Electrochemistry Division to supply fundamentals for a better understanding of the behavior of matter. Such knowledge should eventually lead to new materials of vastly superior properties than those we know today.

While, admittedly, the pursuit of basic research does not guarantee the creation of new and better materials per se, it will provide the possibilities for a real "breakthrough" which is so vital to the realization of our plans 10 to 15 years hence. It eventually may lead to entirely new combinations of matter. For this reason, it is essential that we stimulate interest in basic research.

The future of materials research rests with our members as individuals, but what can we as a Society do to contribute to the solution of the materials problem? Obviously, our first obligation lies in the dissemination of technical and scientific information. We accomplish this, apparently quite successfully, in our meetings. It is due largely to the fortunate combination of engineers, applied and basic scientists in our Society, and their diverse interests in materials that we have witnessed a phenomenal growth in our meetings during the last few years. Six years ago when we met in Washington on the occasion of the 50th Anniversary of the Bureau of Standards, the announcement for the meeting stated: "Of special interest will be the record-breaking number of papers, over 120 titles have been submitted." At this meeting (Washington, 1957) 190 papers are being presented. Our meetings are well attended because they provide an opportunity to discuss not only materials which are available today but also those which are in the development stage and can be brought to the attention of the design engineers for consideration three or five years from now.

New knowledge is gained so rapidly that the need of communication by direct contact among members of the same profession is more important than ever. This is of particular significance today because research is carried out in widely dispersed industrial, academic, and Government laboratories at an accelerated rate. The provision of a platform where material problems can be discussed is of national interest. It gives tremendous moral support to the scientific worker who normally has little opportunity to come in contact with his fellow workers in other laboratories. This applies especially to scientists in the numerous Government laboratories who probably have less opportunity than others to meet their fellow scientists. We are arranging our programs so as to encourage cross-linking of ideas among different fields. It is not always obvious how these fields are mutually interrelated, but combined sessions of various divisions frequently lead to the generation of new approaches which otherwise might be overlooked.

As our meetings take on greater importance, we must also consider them as a means of communication on an international level. The very meeting we are attending is an effort to acquaint ourselves with work going on abroad; we are indebted to our Theoretical Electrochemistry Division and the National Science Foundation for their joint efforts in inviting a number of prominent participants from abroad to the Symposium on Electrolytes. We are honored by their presence and hope that they enjoy their visit with us. We view this as a beginning for similar international symposia in other fields of interest.

Since our obligation is the development of better materials for the National Defense effort, it is also our duty to make known our view that basic fundamental research is the key to better materials. This view, unfortunately, is not as well shared and supported as it should be by our Defense Department. Whereas huge sums are expended on end-items, such as planes and missiles, insufficient funds are available for research, and especially fundamental research. The "Washington Post," a few months ago (February 26, 1957), stated: "Scientists Lose Duel on Weapons," "Many top American scientists have charged that Pentagon research policies neglect basic research. They fear that Russia will outstrip the United States in weapons technology over the long pull because of Pentagon unwillingness to put enough money into searching out new scientific knowledge that might lead to unforeseen technical advances."

It seems to me that it is our duty to stand up against such policy because we know that it will adversely affect our position in the next 10 to 15 years. We need major scientific break-throughs to meet some of the stated requirements for operating conditions, and these can only be expected through intensive research. We also know that it takes years of lead time to transfer a laboratory item into production, and time is therefore of the utmost importance.

We realize that materials are only a means to an end. Not the materials, but the weapons system which will be built with them, will provide our superiority. Only the machines and tools which will be constructed because better and improved materials are available will contribute to our welfare and comfort. It is human nature to admire the final performance, the end result, rather than the labors and tribulations which were necessary to make this final performance a reality. Therefore, let it be our reward to find satisfaction in their use and in the accomplishment of the final objective if we should come up with new and better materials.

This recalls a story about Charles Lawrence, who was the engineer principally responsible for the creation of the Wright Whirlwind Airplane engine which enabled Charles A. Lindbergh to fly nonstop to Paris. In the wake of tremendous hysteria caused by the great event, friends of Lawrence gave him a small dinner honoring him for his forgotten role in the achievement. He said, in responding: "This is nice, and I appreciate it very much, but who the hell ever hears of Paul Revere's horse?"

Our survival as a free nation depends largely on our ability to maintain technical superiority.

The old Latin proverb, "Si vis pacem, para bellum," which says, "If you want peace, prepare for war," unfortunately is still the motto by which we must live.

In a free democracy such as we enjoy, we have an obligation as private citizens, and so have private industry and a Society such as ours, to share the responsibility for preparedness. We cannot just sit still and decide that the Government is solely responsible for solving the materials problem. But, in the final analysis, the new materials which we must develop under the pressure of military necessity eventually will be those which will be used for peaceful purposes and will contribute to the fulfillment of man's hopes for a better world, where weapons are of only secondary importance.

FUTURE MEETINGS OF
The Electrochemical Society

Buffalo, October 6, 7, 8, 9, and 10, 1957

Headquarters at the Statler Hotel

Sessions will be scheduled on
Batteries, Corrosion, Electrodeposition (symposium on "Metal Powders"),
Electrodeposition—Corrosion (Joint Symposium on
"Corrosion of Electrodeposited Metals"),
Electronics (Semiconductors),
Electro-Organics, and Electrothermics and Metallurgy

★ ★ ★

New York, April 27, 28, 29, 30, and May 1, 1958

Headquarters at the Statler Hotel

Sessions probably will be scheduled on
Electric Insulation, Electronics,
Electrothermics and Metallurgy, Industrial Electrolytics,
and Theoretical Electrochemistry

★ ★ ★

Ottawa, September 28, 29, 30, October 1, and 2, 1958

Headquarters at the Chateau Laurier

★ ★ ★

Philadelphia, Pa., May 3, 4, 5, 6, and 7, 1959

Headquarters at the Sheraton Hotel

★ ★ ★

Papers are now being solicited for the meeting to be held in New York, N. Y., April 27-May 1, 1958. Triplicate copies of each abstract (*not exceeding 75 words in length*) are due at the Secretary's Office, 1860 Broadway, New York 23, N. Y., *not later than January 2, 1958* in order to be included in the program. *Please indicate on abstract for which Division's symposium the paper is to be scheduled.* Complete manuscripts should be sent in triplicate to the Managing Editor of the JOURNAL at 1860 Broadway, New York 23, N. Y.

Current Affairs

Further Plans for the Buffalo Meeting

Robert B. MacMullin

Max E. Bretschger

Clifford C. Furnas

Electrochemists attending the 12th Meeting of the Society in Buffalo, October 6 through 10, will enjoy a diversified program of technical sessions and trips. Headquarters will be at the Statler Hotel, on Niagara Square in downtown Buffalo, convenient to the shopping and theater districts.

Your hosts, the Niagara Falls Section, are eager to welcome you to the Niagara Frontier, a major center of electrochemistry and electrothermics. Under General Chairman Robert B. MacMullin, the committee has worked effectively to ensure a smooth-running meeting.

Honorary Chairman of the meeting is Max E. Bretschger, a pioneering leader in electrochemistry. Mr. Bretschger, dubbed "Mr. Peroxide" by the A. I. Ch. E. in testimony to his life's work on hydrogen peroxide, has long been active in The Electrochemical Society.

The program of plant trips is especially extensive and will give plenty of opportunities to see the industries of the area. For the first time, visitors can see the production of zirconium and hafnium, metals of the atomic age. Likewise, leading producers of nickel and of calcium carbide and cyanamid will welcome visiting electrochemists. Those interested in research and development may visit three leading laboratories, one concentrating on aeronautics, one on chemistry, and one on metals and ferroalloys.

Niagara Square in downtown Buffalo. The Hotel Statler is at the right.

The ladies will find that a particularly pleasant variety of tours and events has been planned for them. Mrs. W. C. Gardiner and her committee have made sure that visiting ladies will be able to see the Frontier area at its best. The tour of the Niagara Falls area, with lunch at the beautiful Niagara Falls Country Club, should be particularly memorable.

Reservations—Reservation cards, which have been mailed to all members, should be sent in promptly, direct to the hotel. Be sure to mention The Electrochemical Society.

Technical Program—The complete program of papers, abstracts, symposia, and general information was published in the August issue of the JOURNAL. Carrying on an innovation at the Spring meeting in Washington, no technical sessions have been scheduled for Wednesday afternoon, October 9. This will permit members to take full advantage of the trips to the Niagara Falls area which are scheduled for this afternoon and evening.

Corrosion Division sessions for Tuesday, October 8, will be held at the Sheraton Hotel, on Delaware Avenue, approximately one mile from the Statler Hotel.

Furnas to be Banquet Speaker—Dr. Clifford C. Furnas, Chancellor of the University of Buffalo, and recently Assistant Secretary of Defense for Research and Development, will be the principal speaker at the Palladium Medal Banquet of the Society on Tuesday evening, October 8, in the Ballroom. Dr. Furnas

is nationally known for his accomplishments both as a scientist and as an administrator. He is author of several well-known books, among them "The Next Hundred Years," "Man, Bread, and Destiny," and "The Storehouse of Civilization," and editor of the IRI monograph "Industrial Research—Its Organization and Management." He will draw from his wealth of experience, in charge of Cornell Aeronautical Laboratory, and later of the entire research program of the Department of Defense, to relate government research to industry's needs and growth. This outstanding citizen of Buffalo has richly earned his reputation as a forceful, stimulating public speaker. His talk will be a major highlight of this Annual Meeting and should not be missed.

The Palladium Medalist is the late Dr. Karl Friedrich Bonhoeffer, formerly head of the Max Planck Institute for Physical Chemistry. Because this award is posthumous, the medal will be accepted for Dr. Bonhoeffer by Dr. Paul Harteck who will describe the accomplishments of the medalist.

Battery Round Table

A round-table discussion on fuel cells has been scheduled in the Battery Division program for the fall meeting of the Society in Buffalo for Thursday morning, October 10, at 9 A.M. Mr. G. W. Heise, who will act as Chairman of this discussion, has arranged for several competent workers in this field to lead the discussion.

It is expected that the program will cover a general survey of the current status of fuel-cell investigations in this country as well as in Europe, and its prospects for the future. The following topics will be discussed in detail:

1. Basic aspects of fuel-cell electrodes such as hydrogen, carbon monoxide, hydrocarbon s and oxygen.

2. Systems with aqueous electrolytes including (a) low temperature hydrogen-oxygen cells; (b) high temperature, high-pressure hydrogen-oxygen cell (Bacon); redox systems.

3. Systems with fused-salt electrolytes for the utilization of hydrogen, carbon monoxide, or hydrocarbons and oxygen.

4. General considerations of fuel-cell problems such as potential fields of usefulness of practical systems, fuel sources, and methods of fuel storage.

Highlights of the Board of Directors' Meeting

(Held May 12, 1957, Hotel Statler, Washington, D. C.)

The Board of Directors held its regular meeting on May 12, 1957, prior to the opening of the Washington Convention.

The Treasurer reported that Robert Shannon, the Assistant Secretary, was instrumental in assembling the new form of the Financial Statement which covers the new fiscal year ending March 31, 1957.

Mr. Frank LaQue, Chairman of the Sustaining Membership Committee, recommended that each Division of the Society be represented by a member on the incoming Committee.

He also suggested that a donation be made from Corrosion Handbook Funds to support the work of the Corrosion Research Council, and a contribution of $1,000 was approved for this year, with future donations to be made from the interest from such funds.

The Secretary announced that the Cleveland Section, in accordance with its previously established custom, has this year awarded Student Associate Memberships to Mr. L. L. Schwartz of Western Reserve University and Mr. D. E. Nisbett of Hiram College.

The chartering of new Local Sections in Indianapolis, Columbus, and Mohawk-Hudson (Schenectady) was approved.

It was decided that our Society is agreeable to being recognized as an affiliate of The Institute of Radio Engineers.

Plans for future meetings were discussed, with Mr. MacMullin reporting on the Buffalo Meeting. The Southern California-Nevada Section has agreed to sponsor a meeting in Los Angeles in the Fall of 1962. No decision has been reached concerning a meeting in Indianapolis in the spring of 1961. Dr. Conway discussed the plans for the Ottawa Meeting in the fall of 1958, and Dr. Lowenheim those for the New York Meeting next spring. As customary at New York meetings, there will be no organized plant trips and a minimum of planned entertainment.

The Board approved the submission of the Ways and Means Committee's revised Constitution and Bylaws at the Annual Meeting, May 14, 1957, and recommended this revision for adoption and submission to the mail vote of the membership on the Constitution and adoption of the Bylaws at the next meeting of the Board. The Board expressed its appreciation to Ralph Schaefer and Ralph Hunter for the arduous work performed on this task.

It was voted that we establish reciprocal agreements with The Faraday Society and Deutsche Bunsen-Gesellschaft which would provide that when members of these societies subscribe to our JOURNAL they automatically become members of our Society with the understanding that this reciprocal arrangement would apply only to those individuals living outside of North America.

The Ways and Means Committee also reported that it does not favor increasing membership dues at this time.

Decisions regarding reduced one-day registration fees are to be left to Local Committees.

The revised budget (published here) for the fiscal year April 1, 1957 to March 31, 1958, as recommended by the Finance Committee, was approved.

The President submitted the appointment of Robert J. McKay as Chairman of the Publication Committee succeeding Dr. Robert M. Burns who resigned; and Marvin J. Udy to replace Dr. Burns on the Investment Advisory Panel. These appointments were approved.

The new Becket Award Committee, which consists of G. M. Butler, Chairman (3 years), A. C. Haskell (2 years), and A. T. Hinckley (1 year), reported that announcement of the Becket Scholarship Award had been mailed to various colleges and universities.

It was reported by Dr. Gilbertson, Chairman of the Housing Committee, that the Society offices would move to new quarters at 1860 Broadway, New York 23, N. Y., effective June 1, 1957, with the same useable area. The Committee was discharged with a vote of appreciation.

The Board unanimously voted to reappoint Henry B. Linford as Secretary for another year.

Robert K. Shannon,
Assistant Secretary

Section News

Midland Section

The Midland Section had three Technical Meetings and a Golf Outing and Business Meeting during 1957. On February 5 Mr. Charles Clark from the Power Sources Branch of the Signal Corps Engineering Lab. spoke on "Communications—Type Batteries for Military Use." At the February 20 meeting, Society President Hans Thurnauer gave a talk on "The High Temperature Material Problem." Dr. Milton Stern spoke on "Fundamentals of Corrosion—Some New Ideas" on March 19.

The annual Golf Outing and Business Meeting were held at White Birch Hills, Auburn, Mich. The following officers were elected for the 1957-58 year:

Chairman—H. W. Schmidt, 1313 Helen St., Midland, Mich.
Vice-Chairman—P. F. George, 2905 Manor Dr., Midland, Mich.
Secretary-Treasurer—R. S. Karpiuk, 4608 Bristol Court, Midland, Mich.

P. F. George, *Past Sec.-Treas.*

New York Metropolitan Section

The results of the election of new officers of the New York Metropolitan Section for 1957-58 are as follows:

Chairman—K. B. McCain, Wilbur B. Driver Co., 1875 McCarter Highway, Newark 4, N. J.
Vice-Chairman—G. D. Stendahl, 22 Park Ave., Avenel, N. J.
Secretary-Treasurer—F. S. Lang, International Nickel Co., 63 Linnet St., Bayonne, N. J.

Pittsburgh Section

The Annual June Symposium of the Pittsburgh Section was held on June 14, 1957 at the Alcoma Country Club. The papers presented were: (*a*) "New Thoughts in the Field of Oxidation of Metals" by Earl A. Gulbransen, Westinghouse Research Labs., (*b*) "Measurements to Determine Extent and Distribution of Corrosion" by Melvin H. Brown, Alcoa Research Labs., (*c*) "Current Efficiencies of Magnesium Anodes" by Edson H. Phelps, U. S. Steel Research Labs., (*d*) "Crystal Chemistry" by Albert J. Cornish, Westinghouse Research Labs., and (*e*) "Survey of Methods of Aluminum Plating" by Fred R. Collins, Alcoa Research Labs.

Election of new officers for the coming year was held with the following results:

Chairman—J. J. Stokes, Jr., 134 Station St., Pittsburgh 35, Pa.
Vice-Chairman—Ling Yang, Carnegie Institute of Technology, Pittsburgh, Pa.
Secretary-Treasurer—E. H. Phelps, U. S. Steel Research Lab., Monroeville, Pa.
Representatives on the Council of Local Sections—A. J. Cornish (2 yr) and R. A. Woofter (1 yr).

Ling Yang, *Past Sec.-Treas.*

Ontario-Quebec Section

The fourth and final meeting of the 1956-57 season, held at McGill University, Montreal, on May 3 was well attended. The meeting took the form of a symposium on the topic "Light Metals—Magnesium and Aluminum" and featured a panel of leading authorities from the Canadian light metal industry.

The magnesium panelists were Dr. H. J. W. Lutz, Supervisor, Reduction Development Dept., Aluminum Co. of Canada, Ltd., and Mr. H. G. Warrington, Manager, Sales and Technical Service, Dominion Magnesium Ltd. Dr. Lutz spoke on "The Electrolytic Reduction of Magnesium," while Mr. Warrington's subject was "Man and Magnesium."

The speakers for aluminum consisted of Mr. R. W. Herzer, Member of Staff of General Manager, Aluminum Co. of Canada, Ltd.; Mr. F. R. D.

(Continued on page 200C)

Revised Budget for the Fiscal Year April 1, 1957—March 31, 1958

Income	Budget approved 1/4/57		Revised budget	
General Funds				
Membership Dues	$39,200		$39,200	
Patron & Sustaining Membership	16,000		16,000	
Reprints	4,700		4,700	
Nonmember Journal Subscriptions	22,000		22,000	
Office Sale of Publications & Journal	500		500	
Advertising	12,500		12,500	
Bound Volumes	2,500		2,500	
Conventions	5,300		5,300	
		$102,700		$102,700
Reserve Funds				
Nonmember Journal Subscriptions	$ 4,200		$ 4,200	
Nonmember Convention Registration	2,520		2,520	
Monograph Royalties	6,000		6,000	
Income on Investments	1,800		1,800	
		14,520		14,520
Total		$117,220		$117,220
Expenses				
Printing and Mailing Journal	$40,000		$40,000	
Reprints	2,500		2,500	
Publication Committee	350		350	
Advertising Commission	5,200		5,200	
Salaries, Social Security, & Insurance	42,000		44,500	
Rent	4,000		4,000	
Postage, Supplies, & Miscellaneous	6,200		6,200	
Local Sections & Divisions	1,000		1,000	
Young Author's Prize	100		100	
Reserve New Office Equipment	585		585	
Bound Volumes	3,000		3,000	
Convention Expenses Less Salary Charges:				
Program Booklet	1,580		1,580	
Travel N. Y. Personnel	1,400		1,400	
Materials & Supplies	320		320	
Postage & Express	500		500	
Total Estimated Expenses		$108,735		$111,235
Contingency 1% of Estimated Income		1,027		1,027
Total		$109,762		$112,262
Excess Income Over Expenses, General Fund		−7,062		−9,562
Income Credited to Society Reserve Funds		+14,520		+14,520
Net Excess Income Over Expenses		+7,458		+4,958

Financial Statement of the Electrochemical Society, Inc.

Balance Sheet for Fiscal Period January 1, 1956—March 31, 1957

Statement of Assets

Cash

Chemical Corn Exchange Bank—Main Account			
Corrosion Division Monograph Fund		$ 2,454.68	
Electrothermics and Metallurgy Division Monograph Fund		2,855.45	
Theoretical Division Monograph Fund		328.39	
Electrodeposition Division Monograph Fund		484.47	
F. M. Becket Memorial Award Fund		539.02	
Reserve For New Office Equipment		536.95	
Society Reserve Fund		9,000.09	
General Fund		35,917.46	
		$52,116.51	
Petty Cash—General Fund		68.82	
		$52,185.33	
First National City Bank—General Fund		1,000.00	$ 53,185.33
First National City Bank			
Consolidated Fellowship Fund		21.95	
Guaranty Trust Company			
Edward Goodrich Acheson Fund		1,781.81	
Hanover Bank			
Edward Weston Fellowship Fund		9.31	1,813.07
			$54,998.40

Investments

Edward Goodrich Acheson Fund			
Stocks and Bonds		$32,926.25	
F. M. Becket Memorial Award Fund			
Common Stocks		9,674.00	
Consolidated Fellowship Fund			
Fundamental Investors, Inc.	$12,641.77		
Wellington Fund, Inc.	10,387.44		
Incorporated Investors	1,548.80	24,578.01	
Joseph W. Richards Memorial Fund			
Central Savings Bank		821.62	
Edward Weston Fellowship Fund			
Hanover Trust Fund A—Hanover Bank Trustee		13,787.54	
General Portfolio of Investments (Savings Banks, U. S. Gov't Bonds, Common Stocks)			
Corrosion Division Monograph Fund	$17,195.88		
Columbus Convention Fund	400.00		
Electrodeposition Division Monograph Fund	1,000.00		
Society Reserve Fund	30,517.60	49,113.48	130,900.90

Other Assets

Furniture and Fixtures	5,381.12		
Less Reserve for Depreciation	1,635.70	3,745.42	
Convention Advance (Washington)		500.00	
Guarantee Deposit		400.00	
Inventory		4,760.00	9,405.42
			$195,304.72

Statement of Liabilities and Surpluses

Liabilities

Accounts Payable Suppliers		$ 3,615.08	
Deferred Income India Section		.46	
Overseas Subscriptions Payable (Faraday and DBG)		1,278.00	
Life Memberships		1,457.50	
Prepaid Sustaining Memberships		800.00	
Federal and State Taxes Withheld		644.46	$ 7,795.50

Surpluses

Edward Goodrich Acheson Fund	$34,708.06		
F. M. Becket Memorial Award Fund	10,213.02		
Columbus Convention Fund	400.00		
Consolidated Fellowship Fund	24,599.96		
Joseph W. Richards Memorial Fund	821.62		
Edward Weston Fellowship Fund	13,796.85	84,539.51	
Division Monograph Fund Surpluses:			
Corrosion Division	19,650.56		
Electrodeposition Division	1,484.47		
Electrothermics and Metallurgy Division	2,855.45		
Theoretical Division	328.39	24,318.87	
Society Reserve Fund Surplus:			
Surplus	$28,490.58		
Cash Income Received	11,665.26	$40,155.84	
Less Advances:			
Abstracts of Literature, Semiconductors 1953 Issue	$388.90		
1954 Issue (Credit)	438.00		
	—49.10		
Electro-Organic Chemistry	500.00		
10 Year Index (1952-1961)	187.25	638.15	39,517.69
General Fund Surplus:			
Surplus	$29,940.14		
Reserve for New Office Equipment	536.95	30,477.09	
Excess Income Over Expenses		8,656.06	39,133.15	187,521.12
			$195,316.62

Statement of Income and Expenses for Fiscal Period January 1, 1956—March 31, 1957

	Budget 15 months	General fund	Society reserve fund
Income			
All Membership Dues	$44,250	$45,663.80	
Patron and Sustaining Memberships	19,850	23,300.00	
Reprints	5,000	5,177.50	
Nonmember Journal Subscriptions	34,500	32,691.08	
Office Sale Journal & Publications	1,250	1,491.70	
Advertising	16,000	14,380.18	
Bound Volumes	2,000	2,720.40	
Conventions	3,500	2,964.06	
Membership Directory	400	222.00	
"Cathodic Protection" Sales	250	391.65	
	$127,000	$129,002.37	
Nonmember Journal Subscriptions	5,440		$ 5,064.96
Nonmember Convention Registrations	900		522.00
Monograph Royalties	5,500		5,189.06
Cash Dividends From Investments	500		889.24
	$ 12,340		$11,665.26
	$139,340		
Expenses			
Print & Mail Journal	$44,750	$43,205.02	
Reprints	3,120	2,940.28	
Publication Committee	440	32.00	
Advertising Commissions	6,500	6,656.30	
Salaries	48,750	48,326.26	
Rent	3,000	3,000.00	
Postage, Supplies, & Miscellaneous Expenses	7,715	7,828.84	
Local Sections and Divisions	1,250	851.45	
Young Author's Prize	100	100.00	
Reserve For New Office Equipment	731		
Bound Volumes	4,100	2,605.48	
Membership Directory	750	749.16	
Conventions:			
Program Booklets	1,580	1,442.88	
Travel New York Personnel	1,700	1,734.39	
Materials and Supplies	320	355.10	
Postage and Express	490	519.15	
	$125,296		
Contingency 1% Estimated Income	1,270		
	$126,566	$120,346.31	
Excess Income Over Expenses—General Fund	434	$ 8,656.06	
Income Credited to Society Reserve Fund	12,340	11,665.26	
Total Excess Income Over Expenses	12,774	$ 20,321.32	

Special Funds January 1, 1956—March 31, 1957

Edward Goodrich Acheson Fund

Value of Securities 3/29/57 (Value 1/1/56 $35,503.16)		$32,412.25	
Value New Securities 3/29/57 (Purchase Price September 1956 $418.02)		514.00	
VALUE OF SECURITIES 3/31/57			$32,926.25
Checking Account Balance 1/1/56	$2,240.51		
Cash Income from Investments	1,666.01	$ 3,906.52	
Purchase of New Securities	418.02		
Acheson Medal Award Presentation Expenses at Cleveland Meeting	1,557.17		
Custodian Fees	149.52	2,124.71	
Checking Account Balance 3/31/57			1,781.81
TOTAL FUND VALUE 3/31/57			$34,708.06

Consolidated Fellowship Fund

Fundamental Investors, Inc.

Total Shares 1/1/56 (Value $12,645.92)	722.624	
Shares Accumulated to 3/31/57	84.126	
Total Shares 3/31/57	806,750	
Share Value 3/29/57	15.67	$12,641.77

Wellington Fund, Inc.

Total Shares 1/1/56 (Value $9,958.54)	376.220	
Shares Accumulated to 3/31/57 (Including 379.091 acquired as result of 2 for 1 split)	435.299	
Total Shares 3/31/57	811.519	
Share Value 3/29/57	12.80	10,387.44

Incorporated Investors

Shares Purchased 1/9/57 (Value $1,881.44) from Funds of Edward Weston Fellowship Fund	176.000	
Share Value 3/29/57	8.80	1,548.80
Investment Value Securities 3/29/57		$24,578.01
Checking Account Balance 3/31/57		21.95
TOTAL FUND VALUE 3/31/57		$24,599.96

F. M. Becket Memorial Award Fund

Value of Securities 3/29/57 (Purchase Price June 1956 $10,000.00)		$ 9,674.00
Cash Received from Sale of Rights	$ 308.00	
Cash Dividends from Investments	231.02	539.02
TOTAL FUND VALUE 3/31/57		$10,213.02

Joseph W. Richards Memorial Fund

Central Savings Bank Balance 1/1/56	$ 791.54	
Interest Income to 3/31/57	30.08	
TOTAL FUND VALUE 3/31/57		$ 821.62

(Continued on next page)

General Portfolio of Investments
(Established June 1956)
for Period Ending March 31, 1957

	Purchase or acquired price	Corrosion division monograph fund	Electrodep. division monograph fund	Columbus convention fund	General fund	Society reserve fund
Value of Securities when Purchased or Acquired Indicating Divisional Equity in Portfolio	$45,736.13	$17,195.88	$1,000.00	$400.00	$9,988.63	$17,151.62
New Investments Purchased	1,308.00					1,308.00
Interest Income on Savings Bank Accounts	211.76					211.76
Gifts of Stock to Society	1,935.03				1,074.40	860.63
Additional Accrued Interest on U. S. Govt. Bonds	1,040.00					1,040.00
Dividends Reinvested in Additional Shares of Stock	347.78					347.78
Transfer of Equity in Order to Combine Society Holdings					—11,063.03	11,063.03
	$50,578.70	$17,195.88	$1,000.00	$400.00		$31,982.82
Adjustment in Value of Securities Based on Closing Prices March 29, 1957	—1,465.22					—1,465.22
INVESTMENT VALUE MARCH 31, 1957	$49,113.48	$17,195.88	$1,000.00	$400.00		$30,517.60

NOTES: 1—Any increase or decrease in the value of securities in this Portfolio at the close of our fiscal period is credited or charged to the Society Reserve Fund.
2—Cash Dividends received from Investments in this Portfolio for the period ending March 31, 1957 amounted to $889.24 which has been credited to the Society Reserve Fund.

Edward Weston Fellowship Fund

Value of Shares in Hanover Bank Trust Fund A 3/29/57 (Value 1/1/56 $14,016.97)	$13,715.03	
Principal Account Balance 3/31/57	72.51	$13,787.54
Checking Account Balance 1/1/56	$ 1,314.92	
Income from Investments to 3/31/57	575.83	
	$ 1,890.75	
Purchase of 176 shares of Incorporated Investors for Consolidated Fellowship Fund	1,881.44	
Checking Account Balance 3/31/57		9.31
TOTAL FUND VALUE 3/31/57		$13,796.85

Statement of Auditor

I have examined the balance sheet of The Electrochemical Society, Incorporated, as of March 31, 1957, and the related statement of income and expenses for the period from January 1, 1956, to March 31, 1957. My examination was made in accordance with generally accepted auditing standards, and accordingly included such tests of the accounting records and such other auditing procedures as I considered necessary in the circumstances.

In my opinion, the balance sheet and statement of income and expenses present fairly the financial position of The Electrochemical Society, Incorporated, at March 31, 1957,and its income and expenses for the 15-month period then ended.

(Signed) **H. K. Leicht,** *Auditor*

(Continued from page 197C)

Collin, Manager, General Development and Servicing Div., Aluminum Co. of Canada, Ltd.; and Mr. A. R. Wylie, Plant Manager, Canadian British Aluminum Co., Ltd. Mr. Herzer's topic was "Canadian Experience in the Production of Aluminum," Mr. Collin spoke on "The Future Market for Aluminum," and Mr. Wylie, representing a newcomer to the Canadian aluminum industry, discussed developments leading up to, and the details of, the project at Baie Comeau.

Mr. A. W. Whitaker, Jr., Honorary Chairman of the Section, who recently retired as Executive Vice-President and General Manager of the Aluminum Co. of Canada, was technical chairman for the occasion.

During a short business meeting under the chairmanship of Mr. John Sumner, an interim Treasurer's report was given.

The following were elected officers of the Section for 1957-58:

Honorary Chairman—Prof. J. U. MacEwan, McGill University, Montreal, Que., Canada
Chairman—T. S. Gamble, Electro Metallurgical Co., Toronto, Ont., Canada
Vice-Chairman (Program)—Dr. R. R. Rogers, Dept. of Mines, Ottawa, Ont., Canada
Vice-Chairman (Membership)—H. A. Timm, Dominion Magnesium Ltd., Haley, Ont., Canada
Secretary-Treasurer—L. G. Henry, Box 10, Canadian Industries Ltd., Montreal, Que., Canada
Representatives on the Council of Local Sections—E. A. Hollingshead (1 yr) and L. G. Henry (2 yr)

H. A. Timm, *Past Sec.-Treas.*

Division News

Electric Insulation Division

At the annual business meeting in Washington in May 1957, the following new officers of the Electric Insulation Division were elected:

Chairman—L. J. Frisco, Dielectrics Lab., The Johns Hopkins University, 1315 St. Paul St., Baltimore 2, Md.
Vice-Chairman—A. J. Sherburne,

General Electric Co., 1 River Rd., Schenectady, N. Y.

Secretary-Treasurer — Emanuel Brancato, 3203 Arundel Rd., Mount Rainier, Md.

L. J. Frisco,
Past Vice-Chairman

Electronics Division

The following new officers of the Electronics Division have been elected for two-year terms (1957-59):

Chairman—H. Bandes, Sylvania Electric Products Inc., 100 Sylvan Road, Woburn, Mass.

Vice-Chairman (Luminescence)—R. J. Ginther, Naval Research Lab., Washington 25, D. C.

Vice-Chairman (General Electronics)—C. T. Lattimer, C & P Lab., RCA Victor Div., Marion, Ind.

Vice-Chairman (Semiconductors)—J. W. Faust, Jr., Westinghouse Research Labs., Churchill Borough, Pittsburgh, Pa.

Secretary-Treasurer—M. F. Quaely, 88 Mt. Hebron Road, Montclair, N. J.

Washington-Baltimore Section

The Washington-Baltimore Section held its April meeting in the Pan American Room of the Hotel Statler. Fielding Ogburn, Chairman for the National Convention, and Henry B. Linford, National Secretary, presented plans for the Annual Spring Meeting of the Society to be held on May 12-16, 1957, in Washington. The occasion was used to assign duties to willing helpers. The Ladies, Committee was also in attendance. During the evening the various convention committees held individual meetings.

The Local Section business of the evening consisted of the election of officers for the 1957-58 year. They are:

Chairman—Dr. Ralph Roberts, 3308 Camalier Dr., Washington 15, D. C.

Vice-Chairman—Dr. Gwendolyn B. Wood, National Bureau of Standards, Chemistry Bldg., Rm. 115, Washington 25, D. C.

Secretary—Dr. David Schlain, U. S. Bureau of Mines, College Park, Md.

Treasurer—Dr. Jerome Kruger, 101 N. W. Bldg., National Bureau of Standards, Washington 25, D. C.

Representatives on the Council of Local Sections—Dr. J. C. White and Fielding Ogburn

Gwendolyn B. Wood,
Past Secretary

Battery Division Extended Abstracts Booklet

The Battery Division has prepared an extended abstracts booklet of the 28 papers to be presented at the fall meeting of the Society in Buffalo, October 6-10, 1957.

This bulletin is expected to be available after September 15, at $2.00 per copy, and can be obtained by sending a check to the Secretary of the Battery Division:

E. J. Ritchie
Eagle-Picher Research Lab.
Joplin, Mo.

News Items

Palladium Medal to be Awarded Posthumously to Professor Karl Friedrich Bonhoeffer

At a meeting of the Board of Directors of the Society held in New York in January, it was unanimously voted to present the 1957 Palladium Medal Award to Professor Karl Friedrich Bonhoeffer, Director of the Max Planck Institut für Physikalische Chemie, Göttingen, Germany.

Since this announcement was made Professor Bonhoeffer suffered a heart attack and word was received that in all probability he would be unable to attend the Buffalo Meeting to accept the Award in person. The Board of Directors then decided to make the Award in absentia. Subsequent to this the Society received news of his death.

Professor Bonhoeffer was universally regarded as a scientist of international pre-eminence and his many friends and colleagues in this country and throughout the world will mourn his untimely passing.

In recognition of his outstanding scientific achievements, the 1957 Palladium Medal will be awarded posthumously to Dr. Bonhoeffer at the Buffalo Meeting of the Society this fall. A review of his contributions to electrochemistry will appear in a later issue of the JOURNAL.

NACE Activities to Reach Peak in Fall

With seven major events scheduled in widely separated parts of the United States, the National Association of Corrosion Engineers will reach a peak of activity this fall. These events include, in October: regional meetings at Oklahoma City, Chicago, and San Diego, Calif., and the Seventh Biennial Permina Basin Corrosion Tour at Odessa, Texas. In November: a regional meeting at Pittsburgh. In December: an Underground Corrosion Control Short Course at University of Illinois, Urbana. A second corrosion control short course will be held during October at San Diego, Calif.

The four regional meetings include technical symposia, committee meetings, two regional product exhibitions, and numerous social events. More than 32 technical committees will meet during the regional sessions. Topics of technical interest to be considered include petroleum production and refining, pipelines, industrial coatings, metallurgy, telephone and power cables, process industry corrosion, marine corrosion, cathodic protection, and numerous others.

National Electronics Conference

The 13th annual National Electronics Conference will be held October 7-9 in Chicago at the Hotel Sherman. Approximately 100 technical papers and 240 exhibits will be featured. For additional information on the conference, write to National Electronics Conference, 84 E. Randolph St., Chicago 1, Ill.

New Sustaining Members

P. R. Mallory & Co., Inc., Indianapolis, Ind.; Sprague Electric Co., North Adams, Mass.; and Texas Instruments, Inc., Dallas Texas, recently became Sustaining Members of The Electrochemical Society.

Book Review

An Introduction to Semiconductors by W. Crawford Dunlap, Jr. Published by John Wiley & Sons Inc., New York, 1957, xxi + 417 pages; $11.75.

The author, who is well known for his important contributions in the semiconductor field, has undertaken difficult work, namely to compile in one volume the most useful information on semiconductors. Since this field has seen tremendous growth in recent years, at first glance it might seem hopeless to cover all the subjects listed in the index. However, at a closer view the informed reader is astonished to see how much valuable information is brought together here.

The first six chapters cover a wide range of topics from fundamentals

(Continued on page 209C)

Highlights of the Washington Meeting

A record registration of 1110 at the Washington Meeting marked the first ECS Meeting at which the registration exceeded 1000. It is interesting to note that the large number of papers was not solely responsible for the record attendance. An apparently well-established relationship between the number of papers and the number of registrants fell by the wayside sometime during the third day of registration. The Local Committee is convinced that the best way to estimate the attendance at an ECS Meeting is to ask Henry Linford and he will supply the figure; his method remains a secret.

The 41-technical sessions, sponsored by the Electric Insulation, Electronics, Electrothermics and Metallurgy, Industrial Electrolytic, and Theoretical Electrochemistry Divisions featured 190 papers. The symposium on The Structure of Electrolytes, co-sponsored by the Theoretical Division and the National Science Foundation, brought together the outstanding contributors in this field from all parts of the world.

All of the social functions were well attended and the Monday Evening Mixer proved to be a huge success. Many members will undoubtedly be looking forward to similar events at future meetings.

The ladies, enjoying ideal weather, participated in organized activities which took them through so much of the historic Washington area. Mrs. George W. Vinal, Honorary Chairman of the Ladies' Committee, was unable to attend the meeting and was missed by her many friends, who wish her well.

Those attending the Society Luncheon were treated to an inspiring talk by Dr. Detlev W. Bronk. The Society is indebted to Dr. Bronk for the second of three addresses which he was called upon to deliver that day.

Hans Thurnauer delivered the Presidential Address following the Reception and Banquet on Tuesday, May 14. The Address appears on page 191C of this issue.

Louis J. Frisco, *Chairman*
Washington Meeting
Publicity Committee

Chase Ltd. Photographs

Top row—left, H. T. Francis, J. E. Draley, and Sidney Barnartt; **center,** E. M. Sherwood and Abner Brenner; **right,** Ralph Roberts, W. J. Hamer, and Fielding Ogburn. **Center row—left,** G. W. Vinal and P. L. Howard; **center,** William Blum, Detlev Bronk, and Hans Thurnauer; **right,** candid photo before Society Luncheon. **Bottom row—left,** Dr. and Mrs. A. C. Haskell; **center,** Dr. and Mrs. H. B. Linford, Dr. Sherlock Swann, Jr., Mr. and Mrs. Hans Thurnauer, and Dr. and Mrs. Norman Hackerman; **right,** Dr. and Mrs. T. D. Callinan and Dr. and Mrs. Adolph Gunzenhauser.

The Revised Constitution Needs Your Approval

In recent months the Subcommittee on Constitution and Bylaws of the Ways and Means Committee has been studying revisions of our Constitution and Bylaws in order to provide maximum development opportunities for the Society and remove or revise archaic portions thereof.

Members in attendance at the Annual Meeting held in Washington on May 14, 1957 unanimously approved the submission of the Ways and Means Committee's revised Constitution for a mail vote of the membership of the Society. The revised Constitution is printed below.

On September 15, 1957 a ballot will be sent to voting members of the Society on which they will record their vote for the Election of Officers for 1958 and a space will also be provided on this ballot for members to indicate their vote on these proposed amendents to the Constitution *which shall become effective at the beginning of the fiscal year starting April 1, 1958, upon majority vote of the membership.*

The proposed Bylaws, which will be considered by the Board of Directors at a subsequent meeting, are also printed here in order that members may understand more readily the proposed amendments to the Constitution.

Final Revision of Constitution and Bylaws of The Electrochemical Society, Inc.

Constitution

Article I

NAME AND OBJECT

Section. 1. The name of this organization shall be The Electrochemical Society, Incorporated.

Section 2. The purpose for which it is to be formed is the advancement of the theory and practice of electrochemistry, electrometallurgy, electrothermics, and allied subjects. Among the means to this end shall be the holding of meetings for the reading and discussion of professional and scientific papers on these subjects, the publication of such papers, discussions, and communications as may seem expedient, and cooperation with chemical, electrical, and other scientific and technical societies.

Article II

MEMBERSHIP

Section 1. The individual membership shall consist of active, honorary, and emeritus members. The Board of Directors may from time to time authorize other classifications of membership as defined in the Bylaws of the Society.

Section 2. An active member shall: be interested in electrochemistry or allied subjects; be at least 25 years of age; and possess a Bachelor's or Engineering degree with a major interest in the natural sciences, and have three or more years of postgraduate experience. The degree of Master of Science (or of Engineering) shall be equivalent to one year of experience, and the Doctor's degree in Science (or in Engineering) shall be equivalent to three years' experience. In lieu of a scholastic degree, ten years of experience in electrochemistry or allied subjects shall be required. One year of college work in natural science shall be deemed the equivalent of one year of experience. Election to active membership shall require the recommendation of two active members in good standing.

Section 3. All members in good standing, elected prior to January 1, 1950, became "active" members on that date.

Section 4. Honorary members shall be those individuals who, by reason of valuable contributions to electrochemistry, deserve special recognition by the Society.

Section 5. Any active member who has paid dues for twenty-five years and has attained the age of sixty-five may apply for Emeritus membership. Emeritus members shall pay such dues and registration fees at National Conventions as are set forth in the Bylaws.

Article III

ADMISSION AND DISMISSAL OF MEMBERS

Section 1. Those who prior to April 6, 1902, complied with the membership regulations then in effect are Charter Members of the Society.

Section 2. Application for individual membership shall be in writing on a form adopted by the Board of Directors.

Section 3. The Admissions Committee shall consist of three members appointed by the President with the approval of the Board of Directors for a term of three years. The Committee shall be rotating, with one new member appointed each year to replace the outgoing member. This Committee shall receive from the Secretary all properly executed and properly recommended applications for admission which he has received from persons desirous of becoming members of this Society. It shall be the duty of this Committee, after examining the credentials of applicants, to make appropriate recommendation to the Board as to the fitness of all applicants for membership in this Society. Unanimous approval of an applicant by this Committee shall be required before the candidate's name may be submitted to the Board of Directors for election. The election to membership shall be by a mail vote of the Board of Directors. The candidate shall be considered elected two weeks after the date the proposed membership list is mailed to the Board if no negative votes have been received by the Secretary. If a candidate receives one negative vote, his application shall then be considered and voted upon at a duly called meeting of the Board of Directors. Two negative votes cast at this meeting shall exclude a candidate. The Board of Directors may refuse to elect a candidate who, in its opinion, is not qualified for membership. The names of those elected shall be announced to the Society. Duly elected candidates shall have all the rights and privileges of membership as soon as their entrance fee and dues for the current year have been paid.

Section 4. A member desiring to resign shall send a written communication to the office of the Society.

Section 5. Upon the written request of ten or more active members that, for cause stated therein, a member be dismissed, the Board of Directors shall consider the matter and, if there appears to be sufficient reason, shall advise the accused of the charges against him. He shall then have the right to present a written defense, and to appear in person before a meeting of the Board of Directors, of which meeting he shall receive notice at least twenty days in advance. Not less than two months after such meeting the Board of Directors shall finally consider the case, and if, in the opinion of the majority of the Board of Directors, a satisfactory defense has not been made and the accused member has not in the meantime tendered his resignation, he shall be dismissed from the Society.

Section 6. Corporations, Partnerships, and Individual Proprietorships shall be admitted to membership by the approval of the Board of Directors as defined in the Bylaws.

Section 7. Nominees for Honorary Membership shall be recommended by the Committee of Honors and Awards, and shall be elected to membership by the Board of Directors at a regular meeting, a quorum being present.

Honorary Members shall pay no entrance fee or annual dues, and shall receive the Journal of the Society free of charge.

The number of Honorary Members shall not at any time exceed ten, and not more than two shall be elected in any one calendar year.

Section 8. The entrance fee, annual dues, and any other payments to be made by the members of the Society shall be paid in accordance with regulations set forth in the Bylaws.

Section 9. Any member delinquent in dues after April 1 of each year shall no longer receive the Society's publications, and will not be allowed to vote in any Society election until such dues are paid. All members in arrears for one year after the first of April shall lose their membership status and can be reinstated only by action of the Board of Directors.

Article IV

Officers

Section 1. The Officers of the Society shall be a President, three Vice-Presidents, a Secretary, an Executive Secretary, and a Treasurer. All officers, with the exception of the Executive Secretary, shall be elected. The Executive Secretary shall be appointed by the Board of Directors.

Section 2. Any candidate for elective office shall be an Active Member of the Society who has been a member of the Board of Directors, or who has rendered some signal service to the Society.

Section 3. All elected officers, with the exception of the President, shall hold office for three years; the President shall be elected for one year. Each year a President and one Vice-President shall be elected. At three-year intervals a Treasurer and Secretary shall be elected; the Treasurer's election beginning with the annual meeting of 1949, and the Secretary's election beginning with the annual meeting of 1959. The terms of office of the several officers shall begin at 8:00 A.M. of the last day of the spring meeting or convention prior to which they shall have been elected, and each officer shall hold office until his successor has qualified.

Section 4. No elective officer shall receive, directly or indirectly, any salary, compensation, or emolument from the Society, either as such officer or in any other capacity, or be financially interested, directly or indirectly, in any contract relative to the operations conducted by the Society, or in any contract for furnishing supplies thereto, unless authorized either by the Bylaws or by a vote of the majority of the entire Board of Directors.

Section 5. A vacancy in the office of President shall be filled by the senior Vice-President. All other vacancies shall be filled by the Board of Directors.

Section 6. No revision or amendment of this Constitution shall affect the tenure of office of any duly elected and incumbent officer.

Article V

Election of Officers

Section 1. Before January first of each year the President, with the approval of the Board of Directors, shall appoint a Nominating Committee of five members, not more than two of whom may be officers or directors of the Society. The Nominating Committee shall send to the Secretary before June 15 its nominations for one or more candidates for each of the offices to be filled, except that for the Vice-Presidency at least two persons shall be nominated.

It shall be the duty of the Nominating Committee to notify each candidate of his selection, and any candidate desiring to do so may withdraw his name within one week of such notification.

Section 2. Before July fifteenth, the Secretary shall present the report of the Nominating Committee to the Board of Directors for approval.

Section 3. Before October fifteenth, the Office of the Society shall mail to every Active Member a ballot containing the names of all candidates thus nominated. Biographies of the candidates shall be made available to the membership along with or prior to such mailing. An Active Member's vote for officers shall not be restricted to the nominees whose names appear on the ballot. Only Active Members are eligible to vote, and voting shall be by secret letter ballot; the voter shall sign his name on an outside envelope, and the ballots shall be enclosed in an inner sealed and unmarked envelope.

Voting envelopes much reach the Office of the Society before the fifteenth day of December.

Section 4. Before November 15, the President shall appoint three tellers and three alternates who are not members of the Board of Directors.

Section 5. The Executive Secretary shall deliver to the tellers all valid ballots received at the Office of the Society before December 15. The tellers shall count the ballots and report the results to the President before December 30.

The candidate receiving the greatest number of votes for an office shall be considered elected. The President shall immediately notify all candidates of the results of the election.

Section 6. The President and Vice-Presidents shall be ineligible for immediate re-election to the same office.

Article VI

Management

Section 1. The affairs of the Society shall be managed by a Board of Directors under this Constitution and Bylaws. The Board of Directors shall be composed of the President serving as Chairman, the immediate Past President, the three Vice-Presidents, the Treasurer, the Secretary, two directors to be elected by the Council of Local Sections as provided in Article VII herein, and the Chairmen of the several Divisions of the Society. A majority of the Board membership, represented either in person or by proxy, shall constitute a quorum.

Section 2. The Board of Directors shall prepare and adopt a series of Bylaws which shall govern the Society under this Constitution with respect to its meetings, its procedure, and all other matters not specifically referred to in this Constitution. It shall require a two-thirds roll-call vote of the entire Board to adopt or amend these Bylaws; proxy and mail votes shall be counted when received before the vote is counted. The text of the proposed Bylaws or amendments shall be furnished to each member of the Board of Directors at least ten days before the meeting at which the vote on the same is to be taken.

Section 3. The Board of Directors may delegate any or all of its powers, except in those cases in which the Constitution requires a vote of the entire Board, to an Executive Committee which shall consist of five members from the Board of Directors. The President, Secretary, and Treasurer shall be members of this Executive Committee. This Committee shall conduct the affairs of the Board of Directors between its meetings. All members of the Board of Directors shall receive notice of the meetings of this Executive Committee and its minutes, and shall have the right to attend and vote. A majority of the Executive Committee shall constitute a quorum.

Section 4. The duties of the President, Vice-Presidents, Treasurer, and Secretary shall be such as usually pertain to the offices they hold, besides any other designated in the Constitution or Bylaws or by the Board of Directors. The Secretary shall be in administrative charge to direct and supervise the duties usually pertaining to this office or designated in the Constitution or Bylaws or by the Board of Directors. The Secretary shall, in all matters concerning the affairs of the Society, carry out the prescriptions of the Constitution, Bylaws, rulings, and precedents, and in cases in which no such prescriptions exist, he shall obtain decisions from the Board of Directors, or Executive Committee, or, if time does not permit, he shall

confer with the President. All funds expended in Executive Secretarial duties shall be under the control of the Secretary, who shall be responsible to the Board of Directors for proper expenditure of such funds. The Secretary and the Treasurer shall present reports to the Board of Directors before the annual meeting. The Board of Directors shall present a report to the Society at the annual meeting. The nature of these reports shall be specified in the Bylaws.

Section 5. All standing committees shall be appointed by the President, subject to the approval of the Board of Directors, and shall be responsible to the Board of Directors.

Section 6. Any member of the Board of Directors who finds that he is unable to attend a regularly called meeting of the Board shall have the privilege of appointing a proxy to act in his stead at such meeting. The person appointed to act as proxy shall be an Active Member. No member of the Board shall have the power to grant to any person a proxy for more than one meeting.

Article VII

DIVISIONS AND LOCAL SECTIONS

Section 1. Professional groups representative of the several branches of electrochemistry, to be known as Divisions of the Society and to be organized from its members, may be authorized by the Board of Directors.

Section 2. A Division shall have the right to make rules for its own government, subject to the approval of the Board of Directors, not inconsistent with the Constitution and Bylaws of the Society.

Section 3. The Divisions shall be represented on the Board of Directors by their several Chairmen as provided in Article VI.

Section 4. Members of the Society residing in a given locality may organize themselves into Local Sections, subject to the approval of the Board of Directors. Not more than one Local Section may be organized in a given locality.

Section 5. A Local Section shall have the right to make rules for its own government, subject to the approval of the Board of Directors, not inconsistent with the Constitution and Bylaws of the Society.

Section 6. The several Local Sections shall be organized into a Council of Local Sections. Each Local Section shall be entitled to representation upon the Council. The Council shall make rules for its own government, subject to the approval of the Board of Directors and of the Local Sections represented, and not inconsistent with the Constitution and Bylaws of the Society. The Council of Local Sections shall be entitled to representation on the Board of Directors as provided in Article VI.

Article VIII

MEETINGS

Section 1. The annual business meeting shall be held between April 1 and July 1, at such time and place as the Board of Directors shall designate. Business affecting the organization of the Society shall be transacted only at the annual meetings. Proxy or mail votes shall be honored.

Section 2. Other meetings may be held at such times and places as the Board of Directors shall select. The President shall call a meeting at the written request of thirty or more Active Members.

Section 3. Notice of all ordinary meetings shall be sent to all members at least twenty days in advance, and of the annual meeting, thirty days in advance.

Section 4. Any ten Active Members at a meeting of the Society may require that any motion brought up be submitted to a referendum of the Society by a mail vote.

Article IX

GENERAL

Section 1. A quorum of the Society shall consist of fifty Active Members, present in person or by proxy.

Section 2. Only those Active Members whose dues have been paid for the current fiscal year shall be entitled to vote at any meetings. A member may vote by proxy or by mail. No proxy shall be valid after the expiration of eleven months from the date of its execution. Every proxy shall be revocable at the pleasure of the person executing it.

Section 3. The fiscal year of the Society shall begin on the first day of April and close on the thirty-first day of March in the following calendar year.

Article X

AMENDMENTS

Proposals to amend this Constitution shall be made in writing to the Board of Directors and signed by at least ten Active Members; they shall reach the Secretary not later than February 1. The proposal, with the recommendations of the Board of Directors, shall then be presented to the Society at its annual business meeting. Approval shall require two-thirds majority vote of those in attendance. Final approval shall proceed through mail vote of membership, requiring a majority.

Bylaws

Article I

ORDER OF BUSINESS

Section 1. At the annual business meeting of the Society, the order of procedure shall be as follows:

Approval of the minutes of the the last meeting.
Report of the Board of Directors, including those of the Secretary and the Treasurer.
Reports of Standing Committees.
Deferred Business.
New Business.
Report of Tellers of Election.
Address of the retiring President. (This may be presented at another session of the general meeting at the discretion of the framers of the program of the meeting.)

Section 2. The annual business meeting of the Society shall preferably be on the second day of the general meeting.

Article II

NON-VOTING MEMBERSHIPS

Section 1. Student Member. A Student Member shall be at least eighteen years old, and shall be an undergraduate or graduate student registered for a degree in natural science or engineering. Election to Student Membership shall require recommendation by two Active Members and by a member of the senior staff of the college of his attendance. The Student Member shall submit suitable evidence of graduation to the Executive Secretary's office upon request. Upon graduation from college, unless he enters graduate school, the Student Member shall automatically become an Associate Member at the beginning of the next calendar year. He shall remain an Associate Member for three years and then automatically become an Active Member. When he discontinues graduate studies, he shall automatically become an Associate Member at the beginning of the next calendar year; then an Active Member after the equivalent of three years as Associate Member, each year of graduate study as a Student Member being accepted as a substitute for one year as an Associate Member. All age requirements for Associate and Active Membership shall be waived if the applicant enters the Society initially as a Student Member.

Section 2. Associate Member. An Associate Member shall have received a Bachelor's or Engineering Degree with major interest in natural science, but not yet have completed the requirements of three years' experience, or have exceeded the age of twenty-eight. Election to Associate Membership shall require the recommendation of two Active Members in the Society. No Associ-

ate Membership shall extend beyond the year the holder reaches the age of twenty-eight. An Associate Member shall automatically become an Active Member at the beginning of the next calendar year after he shall have acquired either three years of professional experience or attained the age of twenty-eight, whichever is sooner.

Section 3. Contributing Memberships. Corporations, partnerships, and individual proprietorships who contribute financially to the support and development of the Society shall be entitled to membership which shall be defined by the Board of Directors as either Sustaining or Patron.

Article III

Meetings of the Board of Directors

Section 1. The Board of Directors shall hold a regular meeting immediately preceding each general meeting of the Society.

Section 2. Between said meetings, the Board of Directors may hold special meetings when called by the President.

Section 3. All meetings of the Board of Directors shall be open to Past Presidents. The President shall invite the Chairman of the Publication Committee, and shall have the authority to invite other persons to attend meetings who, in his judgment, will be of assistance to the Board in the transaction of its business.

Section 4. At the regular meetings of the Board of Directors, the order of procedure shall be as follows:

Approval of the minutes of the last regular meeting and of any special meeting, the minutes of which have not been approved.
Appointment of Tellers of Election.
Communications from the President.
Communications from the Treasurer.
Communications from the Secretary.
Discussion of programs of future meetings of the Society.
Reports of Committees.
Deferred Business.
New Business.
Adjournment.

Article IV

Duties of Officers

Section 1. The President shall preside at all business meetings of the Society and at meetings of the Board of Directors. He may represent the Society at any function to which no other particular delegate has been appointed by the Society or the Board of Directors.

Section 2. The Secretary, besides performing the usual duties of that office, shall be the guardian of the records of the Society, collect dues from members, all bills owing to the Society, and pay such amounts to the Treasurer. He shall report to the Board of Directors at each of its meetings on the condition of the affairs of the Society. In addition, the Secretary shall be a member of the Publication Committee.

Section 3. The Executive Secretary shall be responsible to the Secretary, and shall perform such duties as are delegated to him by the Secretary.

Section 4. The Treasurer shall report to the Board of Directors at its meeting immediately preceding the business session of the annual meeting of the Society on the condition of the finances of the Society, and make such recommendations as will, in his opinion, tend to safeguard or improve the same.

Section 5. The Board of Directors shall report at the annual meeting on the general affairs of the Society.

Section 6. Funds budgeted for operation of the Society shall be disbursed on checks signed by any two of the following three officers: Executive Secretary, Secretary, or Treasurer, or their agents as authorized by the Board of Directors. For disbursal of budgeted expenditures they may establish agents' funds which are under the control of the Secretaries.

Article V

Standing and Special Committees

Section 1. The following Standing Committees shall be maintained in addition to the Admissions Committee established under Article III, Section 3, of the Constitution: Publication, Ways and Means, Finance, Membership (Personal and Contributing), Honors and Awards, Palladium Medal Award, F. M. Becket Memorial Award, and Investment Advisory Panel.

Section 2. The President may appoint special committees to conduct investigations or to represent the Society on special occasions.

Section 3. Unless otherwise specified, all committee appointments shall expire with the term of the President who made the appointments.

Section 4. Each committee shall submit an annual report to the Board of Directors of its activities.

Article VI

Publications

Section 1. A Publication Committee shall be appointed for a three-year term by the Board of Directors. The Committee shall consist of a Chairman, the Secretary of the Society, and the Editor of the Journal. This committee shall be responsible to the Board of Directors for the financial and managerial policy of all Society publications.

Section 2. Journal of the Society. Effective January 1, 1948, there is established a monthly publication of the Society to be called "Journal of The Electrochemical Society."

Section 3. Editorial Board of the Journal. The Editor shall be Chairman of the Editorial Board whose membership shall include the Managing and News Editors of the Journal and the Chairman of the Publication Committee. They shall determine editorial policy within the framework of the managerial and financial policy described by the Publication Committee.

Section 4. Divisional Editors of the Journal. The Editor of the Journal, with the approval of the Editorial Board, shall appoint Divisional Editors for three-year terms with the advice and knowledge of the Chairmen of the respective Divisions. The Editor shall arrange with the Divisional Editors for a review of all papers submitted for publication. Acting within the policy of the Publication Committee, he shall have the authority to accept or reject any submitted paper, and to select the technical articles for the Journal.

Section 5. Financing of the Journal. Each year the Board of Directors shall, upon the advice of the Finance Committee, set up a budget to cover all expenses of the Journal. The Publication Committee shall operate the Journal within this budget, subject to a review of its operation at each and every meeting of the Board of Directors. Warrants for the payment of bills from the fund thus set up shall be signed by the Treasurer and Secretary, and shall be disbursed from the funds of the Society by the officers empowered to disburse the Society funds.

All income to the Journal from advertising and sales of subscriptions shall be received into the General Fund of the Society by the Executive Secretary.

Section 6. Monographs and Special Publications. Interested individuals or groups wishing to publish within the monograph series of the society shall obtain approval from the Board of Directors, acting on the advice of the Publication Committee. The Publication Committee shall establish the mechanics and format of publication.

Article VII

Ways and Means Committee

Section 1. The Ways and Means Committee shall act as an advisory group to the President and Board of Directors on all phases of the Society's business.

Section 2. The Ways and Means Committee shall be composed of seven members. Its Chairman shall be one of the Vice-Presidents. The other members shall be the two remaining Vice-Presidents, and four members shall be appointed by the President from the active membership of the Society with the approval of the Board of Directors.

Section 3. The Ways and Means Committee may carry on its business through subcommittees composed of

a Chairman, who shall always be a member of the Committee, and such other members of the Society at large as the Chairman of such subcommittees may select.

Section 4. The Ways and Means Committee shall have the power to call on any of the officers of the Society or of its Sections or Divisions to furnish this Committee with such information as it may deem necessary competently to advise the President and Board of Directors as to policies to be followed in the conduct of the Society's affairs.

Section 5. The Ways and Means Committee shall report at appropriate intervals to the President and Board of Directors upon such items of the Society's business as have been referred to this committee for attention.

Article VIII

Finance Committee

Section 1. The Finance Committee of five members shall be appointed by the President with the approval of the Board of Directors. This committee shall consist of the Treasurer who shall be Chairman, the Secretary, at least one Vice-President who is Chairman of the Ways and Means Committee, and two other members appointed from the active membership.

Section 2. The Finance Committee shall assist the Board of Directors in the preparation of a budget and advise the Board on matters of income, expense, and investment of all funds, and all other financial operations of the Society.

Article IX

Membership Committees

Section 1. Personal Membership Committee. The President shall appoint, with the approval of the Board of Directors, a Personal Membership Committee consisting of one representative from each Division and one from each Local Section of the Society. The selection of these members shall be from a list of nominees submitted by each Division and Local Section respectively. The President shall, with the approval of the Board of Directors, appoint a Chairman of the Personal Membership Committee.

Section 2. Contributing Membership Committee. The President shall appoint, with the approval of the Board of Directors, a Contributing Membership Committee to solicit Sustaining and Patron memberships from industry. The President shall, with the approval of the Board of Directors, appoint a Chairman of the Contributing Membership Committee.

Article X

Committee for Honors and Awards

Section 1. The Honors and Awards Committe shall be appointed by the President with the approval of the Board of Directors, and shall be organized and operated in accordance with the rules and regulations adopted at the Directors' meeting on March 3, 1949, governing the award of the Edward Goodrich Acheson Medal and Prize.

Section 2. Acheson Award. The Honors and Awards Committee shall make recommendations to the Board of Directors for Acheson Medalists in accordance with the rules and regulations adopted by the Board of Directors on March 3, 1949.

Section 3. Honorary Members. The Honors and Awards Committee shall make recommendations to the Board of Directors for Honorary Membership in the Society of individuals who, in the opinion of the Committee, have made valuable contributions to electrochemistry or who deserve special recognition by the Society.

Section 4. Palladium Medal Award. The Palladium Medal shall be awarded by the Palladium Medal Award Committee which shall be selected and which shall function in accordance with the rules and regulations approved by the Board of Directors on October 9, 1955.

Section 5. F. M. Becket Memorial Award. The F. M. Becket Memorial Award shall be awarded by the F. M. Becket Memorial Award Committee which shall be selected and which shall function in accordance with the rules and regulations approved by the Board of Directors on October 9, 1955.

Section 6. The Honors and Awards Committee shall, at the direction of the President with the approval of the Board of Directors, make recommendations for other awards and honors not otherwise designated in the Constitution and Bylaws. It shall be authorized to receive suggestions from the membership as to all awards under its jurisdiction.

Article XI

Investment Advisory Panel

Section 1. The Investment Advisory Panel shall consist of five members appointed by the President with the approval of the Board of Directors for a term of five years. The Panel shall be rotating, with one new member appointed each year to replace the outgoing member, and it shall elect its own Chairman.

Section 2. It shall be the responsibility of this Panel to review the investments of the Society annually, and to make suitable recommendations to the Treasurer, as Chairman of the Finance Committee, for appropriate revisions of the Society's investment portfolio.

Section 3. The Treasurer of the Society shall have the responsibility of reviewing and implementing the Panel's recommendations, and of informing the Panel what additional monies have become available for investment.

Section 4. The Board of Directors is responsible for the judicious handling of the Society's assets. However, in the interest of expeditious operation it may delegate to the Treasurer, with the advice of the Investment Advisory Panel, the execution of its investment policy.

Article XII

Programs

Papers, abstracts, reports, and any material given at the technical sessions of the Society shall be assembled by the joint action of the officers of the Divisions and the Secretary of the Society.

Article XIII

Accounts of the Society

The Board of Directors shall engage a public accountant, not later than March 15th each year, to audit the current accounts and financial statements of the Society. The report of such accountant shall be submitted in such form as to designate the source of all receipts by the Society and the disposition of all funds expended. It shall also include, as far as possible, a statement of the assets and liabilities of the Society so drawn up as to show clearly the net worth of the Society as of March 31st of the year for which the audit is made. The report of the auditor shall be submitted to the Board of Directors through the Treasurer of the Society.

In lieu of this report the financial statement and a statement of examination by the Auditor may be printed in the Society's Journal not later than two months after its approval by the Board. The general results of this audit shall be reported to the members of the Society at the annual meeting.

Article XIV

Guests at Meetings

Nonmembers may attend technical meetings and social functions of the Society. Requirements for registration of nonmembers may be established by the Local Committee in charge of said functions with approval of the Board of Directors.

Article XV

Divisions

Section 1. Any member of the Society may register for membership in any Division.

Section 2. The Officers of the Division shall be a Chairman, one or more Vice-Chairmen, and a Secretary and a Treasurer. The Offices of Secretary and Treasurer may be held by the same person. The above officers, together with two or more members of the Division, shall constitute the Executive Committee of the Division.

The Division shall elect its officers and other members of the Executive

Committee during a general meeting of the Society or within thirty days thereafter. The officers and other committee members shall be elected for such terms as the Division Bylaws provide, these terms of office not to exceed two years. An officer may be re-elected, however, if the Division Bylaws do not prohibit such re-election.

Section 3. A Division shall hold, if possible, one session a year at a general meeting of the Society, such session to be under the auspices of said Division, and publication of papers for such sessions to be subject to the usual regulations and control of the Publication Committee.

Section 4. The Society shall not be responsible for any debts contracted by the Divisions or by the officers thereof. Divisions may receive from the Society such financial assistance as the Board of Directors may determine to be proper, provided such request is accompanied by a financial statement covering the previous fiscal year. It is recommended that each Division submit a financial report within three months of the close of its fiscal year. Such funds shall be used for sending out notices, for solicitation of papers, and for the legitimate work of the Divisions.

Section 5. The Board of Directors may recommend the dissolution of any Division of the Society, such recommendation to be submitted to a vote of the members present at an annual business meeting of the Society.

Section 6. Divisions shall have the privilege of suggesting to the Secretary the names of eligible candidates for officers of the Society. Such suggestions shall be in the hands of the Nominating Committee prior to April 1 each year. The Secretary shall transmit such suggestions to the Chairman of the Nominating Committee when he has been selected.

Section 7. It shall be the duty of the Executive Secretary of the Society to call to the attention of the officers of each Division all of the provisions of Article XV at least once between January 1st and April 1st each year.

Article XVI

Regulations Concerning the Formation and Conduct of Local Sections

Section 1. Geographic boundaries of the several Local Sections shall be set from time to time by the Board of Directors upon the advice of the Council of Local Sections. Members of the Society living or having their principal place of business within said boundaries shall be members of the appropriate Local Section, provided they comply with the regulations of the said Section. Members of the Society may become affiliated with any Section upon application to the Secretary of that Section. Only members of this Society are eligible for membership in the Local Sections.

Section 2. The following provisions shall apply to financial matters of common interest to the Local Section and the Society: (1) The expenses of each Local Section shall be borne by the members enrolled in said Section. The Society shall not be responsible for any debts contracted by a Local Section or by the Officers thereof. Exceptions can be made only in the case of General Meetings for which the Local Section acts as host, as provided in Section 5. (2) Local Sections submitting proof of at least three technical meetings during the fiscal year of the Society will thereupon be granted a sum of fifty dollars each as financial assistance.

Additional financial assistance up to fifty cents per member may be provided by the Society in each fiscal year, provided the Local Section raises an equal amount from local dues, assessments, or transfer of funds from inactive accounts. Such additional assistance will be made only upon written request of the Local Section, accompanied by a financial statement. This financial statement is due within three months of the close of the fiscal year of the Section.

(3) Local Sections will receive one dollar from the initial dues of a new member, such sum to be sent to the Local Section by the Executive Secretary of the Society, provided the Local Section was active in securing said new members. To obtain credit for new members, the application must be forwarded to the Executive Secretary of the Society by the Secretary of the Local Section.

Section 3. Each Local Section shall transmit promptly after each meeting to the Executive Secretary of the Society an abstract of its proceedings, including the titles and names of authors of all papers read before it.

Section 4. When a Local Section acts as host for a general meeting of the Society, it shall elect one of the following two plans for handling finances of such meetings and shall so advise the Executive Secretary of the Society not less than 90 days prior to the opening of such meeting.

Plan A. The Local Section assumes full responsibility for handling finances of the general meeting, is responsible for all debts, and shall divide any surplus funds after the payment of all convention expenses and the Society's per capita tax on registrants as determined by the Board of Directors. This division of surplus funds shall be on the basis of a sliding scale as listed below.

Amount of Surplus	National Office Share	Local Section Share
First $500	$ 0	$500
Next $1000	500	500
Next $1000	750	250
Anything Over $2500	90%	10%

Local Sections shall submit a complete financial report to the Executive Secretary of the Society as soon as possible after the close of the meeting, and in case of a deficit shall notify the Executive Secretary when said deficit has been discharged.

Plan B. The Local Section assists the Board of Directors and the Executive Secretary of the Society in handling the finances of the meeting in its territory, but makes no financial arrangements without the general approval of the Executive Secretary of the Society; the Society shall be responsible for any deficit and shall retain any surplus.

Section 5. Before July 1st each year, each Section shall appoint or elect a Councilor to the Council of Local Sections. Such Councilor shall be an Active Member in good standing in the Society, and shall hold office for two years, beginning on July 1st immediately following his or her election, and each Section shall be entitled to two such Councilors. In addition, members of the Society not attached to any Local Section may be placed on the Council by petition of ten members of the Society. Not more than two such Councilors-at-Large may hold office at any one time. Such Councilors-at-Large cannot be from any one locality for more than one two-year term in succession unless a Local Section has been formed in the interim and they thus become regular councilors.

Section 6. The Council of Local Sections shall hold a meeting at each general meeting of the Society. The duties of the Council of Local Sections shall be: (1) to consider problems affecting the welfare and operation of the Local Sections and to work toward their solutions, (2) to act as a clearing house on information, problems, and methods of organization of Local Sections, (3) to act as an advisory council to the Board of Directors of the Society on Local Section affairs, and (4) to make recommendations to the Board of Directors on such other matters relating to the interests of the individual members of the Society as the Councilors may become aware of from time to time.

Section 7. The Council of Local Sections shall elect one of its Local Section Councilors to the Board of Directors at each Spring Meeting of the Council for a two-year term, and he will be seated immediately at the next meeting of the Board of Directors. During the period a Councilor is a member of the Board of Direc-

tors he shall continue to be a member of the Council. The Council shall also elect a Chairman, Vice-Chairman, and Secretary from its Local Section Councilors to conduct the necessary meetings and correspondence of the Council. Bylaws approved by the Board of Directors shall guide the formation and operation of the Council.

Section 8. Local Sections shall have the privilege of suggesting to the Secretary the names of eligible candidates for officers of the Society. Such suggestions shall be in the hands of the Nominating Committee prior to April 1 each year. The Secretary shall transmit such suggestions to the Chairman of the Nominating Committee when he has been selected.

Section 9. It shall be the duty of the Executive Secretary of the Society to call to the attention of the officers of each Local Section all of the provisions of Article XVI at least once between January 1st and April 1st each year.

Article XVII

Dues and Fees

Section 1. The annual dues for Active Members shall be fifteen dollars, of which five dollars shall be a nondeductible subscription to the Journal of The Electrochemical Society. The annual dues for Student Members shall be three dollars, and for Associate Members nine and a half dollars. Each Student Member and each Associate Member shall receive the Journal of The Electrochemical Society. The subscription price of the Journal of The Electrochemical Society to nonmembers shall be set annually before November 1 by the Board of Directors.

Section 2. Any Active Member of the Society who shall pay $300 at one time shall be exempt from the payment of any further dues, and shall be considered an Active Member during the remainder of his life.

Section 3. Corporations, partnerships, and individual proprietorships to qualify for membership in the Society shall contribute at least $100 per annum.

They shall be credited with multiple memberships for each $100 they contribute, and shall be called Sustaining Members. Those who contribute at least $1,000 per annum to the Society shall be designated as Patron Members.

Sustaining Members holding one membership only shall be entitled to designate an employee for membership in the Society. This individual shall be, while supported by the Sustaining Member, entitled to the grade for which he qualifies. The Sustaining Member shall receive one subscription to the Journal and one bound volume, and is free to designate the individual or organization which shall receive it.

Corporations, partnerships, and individual proprietorships holding multiple Sustaining Memberships shall be entitled to designate two employees for membership, and shall be entitled to receive one subscription to the Journal and one bound volume for each Sustaining Membership.

Corporations, partnerships, and individual proprietorships holding Patron Membership shall be entitled to designate two employees for membership, but they shall be entitled to at least two subscriptions to the Journal and at least two bound volumes, and more upon request up to the total number of ten.

Section 4. Emeritus Members shall be exempt from the payment of annual dues and shall receive the Journal of The Electrochemical Society without charge.

Section 5. Society Divisions and Local Sections may collect Division or Section dues as authorized by their respective Bylaws.

Article XVIII

Appeals

Appeals from decisions of the Secretary, Publication Committee, or Division Officers may be made in writing by any member to the Board of Directors, which has the power to alter or confirm the appealed decision.

Article XIX

Amendments

Amendment to these Bylaws may be proposed by the Board of Directors and shall require a two-thirds roll-call vote of the entire Board for their adoption; proxy and mail votes shall be counted when received before the vote is counted. The text of the proposed amendments shall be transmitted to each member of the Board of Directors at least ten days before the meeting at which the vote on the same is to be taken.

Book Review

(Continued from page 201C)

of crystal structure and analysis, energy band theory, imperfections, and statistical mechanics to the electron theory for metals and semiconductors. Chapter 1 introduces a number of important notations and definitions. Chapter 2 is a short survey on a few basic crystal structures. In Chapter 3, energy bands are introduced and some elements of wave mechanics are discussed, including the Kronig-Penney potential model. The effective mass tensor is defined from the expression for the velocity of an electron wave packet. In Chapter 4 the major crystal imperfections are discussed, the part dealing with dislocations being rather outdated. In Chapter 5, the three basic statistics are introduced and a nice argument leads the reader from the expression of the Fermi energy in metals to the semiconductor and the thermionic cathode. Recombination processes and noise problems receive very short mention. More space is given to the electron theory of metals and semiconductors. The Lorentz and Gans solution of the distribution function is outlined. A useful compilation of the different scattering mechanisms concludes Chapter 6.

The following Chapters, 7 and 8, on contacts, surfaces and *p-n* junctions, begin the more general introduction into the device field with some familiar diode equations (Torrey-Whitner) and junction equations (Shockley). Chapter 9 outlines a few important measurement methods for resistivity, mobility, and lifetime. Some technological detail is given which may be of much help to those not specialized in this field. The same is true for Chapter 10 on crystal growth.

In Chapter 11 the reader finds a more detailed compilation of the properties of germanium and silicon with a reproduction of numerous charts from the literature. One may find here: temperature dependence of resistivity and Hall coefficient for different impurity densities, ionization energies, magnetoresistance, and diffusion. This and Chapter 12, with similar data on compound semiconductors, will be helpful for the semiconductor engineer. The description of rectifiers (Chapter 13) and transistors (Chapter 14) is very general since, along with definitions, it also discusses production methods, characteristics, and design data. The final chapter deals with photocells, thermistors, Hall-generators, particle counters, cathodes, and phosphors in 28 pages.

While it is obvious that many topics are only mentioned, this book can be considered as an excellent treatise in the frame of the author's scope, namely, to introduce engineers, technicians, and research workers to one of the most extended fields in modern physics.

H. F. Mataré

Employment Situations

Positions Available

PHYSICAL-ELECTROCHEMIST

Ph.D. with 1-3 years' experience. Interested in electrochemical process research. Responsible for planning and directing process improvement program on electrolytic caustic-chlorine cells. Senior project chemist level supervising other chemists and technicians.

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Westvaco Chlor-Alkali
Division
Food Machinery and Chemical
Corporation
South Charleston, W. Va.

Electronic Scientists, Metallurgists, Physicists, Technologists, and **Engineers** (Aeronautical, Electrical, Electronic, Industrial, General, Mechanical, and Power Plant). The Naval Air Material Center, Philadelphia 12, Pa., has an urgent need for qualified engineering and scientific personnel to fill vacancies in the above positions. The Center is currently engaged in an extensive program of aeronautical research, development, experimentation, and test operations for the advancement of Naval aviation. Starting salaries range from $4480 to $7570 per annum. Application for Federal Employment, Standard Form 57, should be filed with the Industrial Relations Dept., Naval Air Material Center, Naval Base, Philadelphia 12, Pa. Applications may be obtained from the above address or information as to where they are available may be obtained from any first or second class post office.

Meetings of Other Organizations

Sept. 8-13—American Chemical Society, National Meeting, New York, N. Y.

Sept. 15-18—American Institute of Chemical Engineers, Regional Meeting, Lord Baltimore Hotel, Baltimore, Md.

Advertisers' Index

Bell Telephone Laboratories, Inc. 187C
Continental Can Company, Inc. 210C
Dow Chemical Company 186C
E. I. du Pont de Nemours & Co. (Inc.) 190C
Enthone, Incorporated ..... Cover 4
Great Lakes Carbon Corporation ..... Cover 2
Stackpole Carbon Company 189C

Oct. 1-4—National Association of Corrosion Engineers, North Central Regional Meeting, Chicago, Ill.

Oct. 1-4—National Association of Corrosion Engineers, South Central Regional Meeting, Oklahoma City, Okla.

Oct. 7-9—National Association of Corrosion Engineers Northeast Regional Meeting, Pittsburgh, Pa.

Nov. 13-15—American Standards Association, Annual Meeting and National Conference on Standards, St. Francis Hotel, San Francisco, Calif.

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The Electrochemical Society

INSTRUCTIONS TO AUTHORS OF PAPERS

Address all correspondence to the Editor, JOURNAL OF THE ELECTROCHEMICAL SOCIETY, 1860 BROADWAY, NEW YORK 23, N. Y.

FORM

Manuscripts submitted for publication should be in triplicate to expedite review. They should be typewritten, double-spaced, with 2½-4 cm (1-1½ in.) margins.

Title should be brief, followed by the author's name and his business or university connection.

Abstract of about 100 words should state the scope of the paper and give a brief summary of results.

ILLUSTRATIONS

Drawings will be reduced to column width, 8.3 cm (3¼ in.), after reduction should have lettering at least 0.15 cm (1/16 in.) high. Original drawings in India ink on tracing cloth or white paper are preferred. Curves may be drawn on coordinate paper only if the paper is ruled in blue. All lettering must be of lettering-guide quality. See sample drawing on reverse page.

Photographs must be glossy prints and mounted flat.

Captions for all figures must be included on a separate sheet. Captions and figure numbers should not appear in the body of the figure.

General—Figures should be used only when necessary. Omit drawings or photographs of familiar equipment. Figures from other publications are to be used only when the publication is not readily available, and should always be accompanied with written permission for reprinting.

REFERENCES

Literature and patent references should be listed at the end of the paper on a separate sheet, in the order in which they are cited. They should be given in the style adopted by *Chemical Abstracts*. For example:

R. Freas, *Trans. Electrochem. Soc.*, **40**, 109 (1921).

H. T. S. Britton, "Hydrogen Ions," Vol. **1**, p. 309, D. Van Nostrand Co., New York (1943).

H. F. Weiss (To Wood Conversion Co.), U. S. Pat. 1,695,445, Dec. 18, 1928.

UNITS OF MEASUREMENT

Metric units should be used throughout but, where desirable, English units may be given in parentheses.

Corrosion rates in the metric system should preferably be expressed as milligrams per square decimeter per day (mdd), and in the English system as inches penetration per year (ipy).

As regards algebraic signs of potentials, the standard electrode potential for $Zn \rightarrow Zn^{++} + 2e$ is negative; for $Cu \rightarrow Cu^{++} + 2e$, positive.

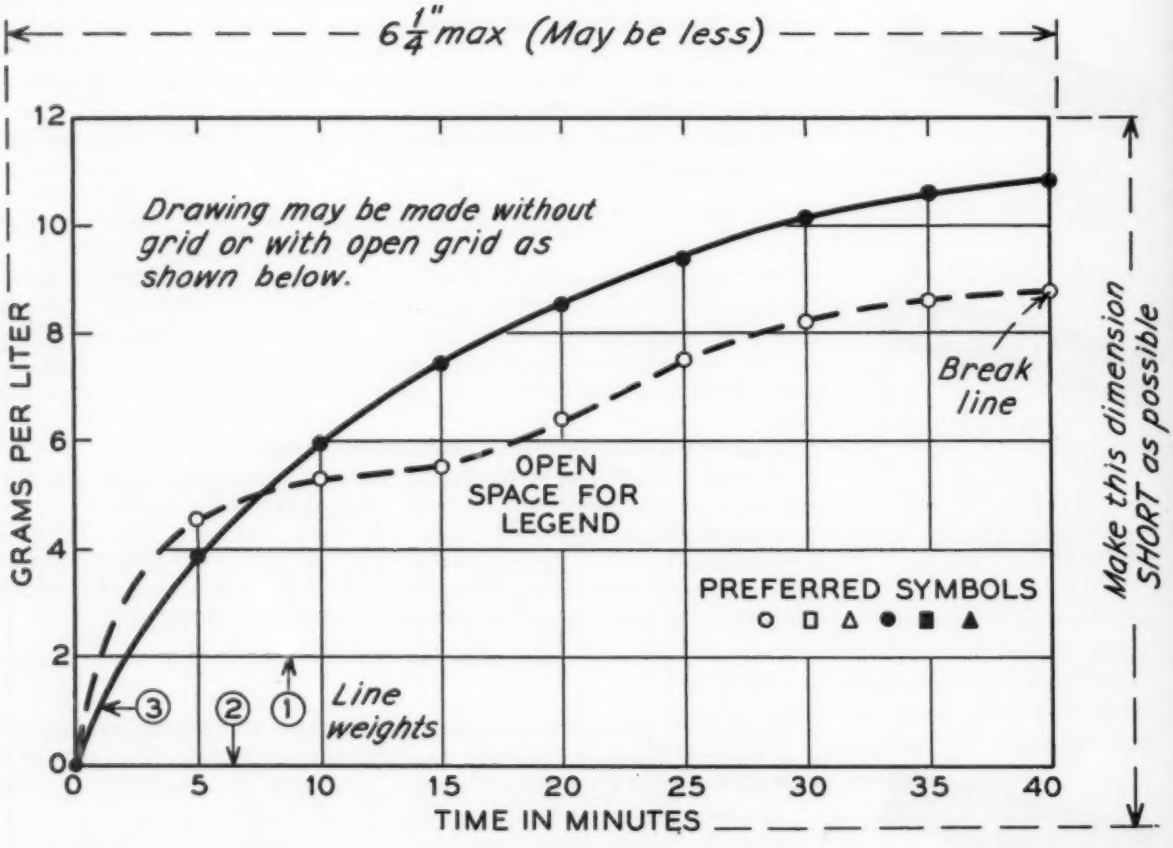
ABBREVIATIONS

Abbreviations should conform with the American Standards Association's list of "Abbreviations for Scientific and Engineering Terms."

GENERAL

Authors should be as brief as is consistent with clarity, and must omit all material which can be regarded as familiar to specialists in the particular field.

The use of proprietary names, trade-marks, and trade names should be avoided if possible. If used, these should be capitalized so that the owner's legal rights are not jeopardized.



Remarks: Line weight ② is used for borders and zero lines. When several curves are shown, each may be numbered and described in the caption. Lettering is approx. 1/8".

SAMPLE CURVE DRAWING FOR REDUCTION TO $\frac{1}{2}$ SIZE